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RESEARCH PAPERS

FROM THE

KENT CHEMICAL LABORATORY

OF

YALE UNIVERSITY

EDITED BY

FRANK AUSTIN GOOCH

Professor of Chemistry in Yale University

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A TRIBUTE TO THE MEMORY

OF

ALBERT EMMETT KENT

PREFATORY NOTE

THIS volume is a record of research carried on in the Kent Chemical Laboratory of Yale University from the opening of the laboratory in 1888 to the present time. It is made up, for the most part, of articles which have appeared from time to time in the *American Journal of Science*, of a few papers issued originally in the *American Chemical Journal*, and of a few studies as yet unpublished elsewhere.

The previously published subject-matter is reproduced in essentially its original form, with, however, occasional slight verbal changes and corrections, and a few abridgments. The arrangement of the material, and of the Table of Contents, generally follows the order of production. A classification by topics is presented in the Systematic Index which precedes the Index of Authors and the Index of Subjects.

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RESEARCH PAPERS

FROM THE

KENT CHEMICAL LABORATORY OF YALE UNIVERSITY

RESEARCH PAPERS

I

A METHOD FOR THE DETERMINATION OF IODINE IN HALOID SALTS.

By F A. GOOCH and P. E. BROWNING.*

Few problems of analysis have been more discussed than the estimation of iodine accompanying chlorine and bromine in haloid salts; and yet the constant succession of new processes is sufficiently indicative that the solution of the question is not generally regarded as satisfactorily settled. The method of Fresenius, according to which iodine is liberated by nitrous acid, collected in carbon disulphide and titrated by sodium thiosulphate, finds ready acceptance for the determination of small amounts of iodine; but when the quantity of iodine to be estimated is considerable, the method is unwieldy. Probably the process most generally in use is that based upon the liberation of iodine by means of a ferric salt, and the titration of the distillate by one or other of the well-known iodometric methods. The latter method is fairly accurate, but the requirement of special apparatus for properly condensing the distillate is detrimental to rapidity and ease of execution. In this process the amount of iodine set free should be measured exactly by the reduction of the ferric salt, and, were the ferrous salt produced in the course of the action sufficiently stable, the determination of its amount might be substituted for the titration of the iodine, and so the collection and further treatment of the distillate might be dispensed with; but ferrous salts are too sensitive to atmospheric influence to preserve under the conditions of this process their own degree of oxidation, and

* From the American Journal of Science, xxxix, 188.

the amount of iron found in the ferrous condition cannot be made to serve as a trustworthy indication of the reducing action which actually takes place in the separation of the iodine. The advantage of replacing the collection and examination of the distillate by treatment of the residue is, however, so great as to constrain us to search for some substitute for the ferric salt, which, by virtue of easy reducibility may act as a liberator of iodine from hydriodic acid, and, at the same time, by reason of stability after reduction, shall register accurately the quantity of iodine set free in the reducing process. The results of our experience are contained in the following account.

Strong sulphuric acid, as is well known, acts upon an iodide in a way to liberate iodine at the cost of its own loss of oxygen, though by simple dilution of the mixture thus formed the action is reversed, the iodine going back into the form of hydriodic acid, and the products of the reduction of sulphuric acid again taking back their oxygen and re-forming the acid. In the presence of any substance easily reducible by the deoxidation products of sulphuric acid, the liberation of iodine by the action of that acid upon iodides should take place without interference, and even more easily and completely than in the absence of such a substance, while the sulphuric acid should remain at the end of the process in its original form. If the products of reduction which appear in such a case in the place of those of the sulphuric acid should be neither readily oxidizable nor easily volatilizable, it ought to be possible to remove by heat the iodine set free in the action without disturbing the record kept of its amount by the reduced substance remaining in the residue.

The qualities of arsenic acid suggest it as a substance likely to possess just these qualities; for, though arsenious acid is converted into arsenic acid by the action of iodine in alkaline solution, in acid solution the reverse is true to at least a limited extent, and arsenic acid liberates iodine according to the equation,

$$H_3AsO_4 + 2HI = H_3AsO_3 + H_2O + I\text{-}I.$$

In company with sulphuric acid of such strength as to liberate the iodine from hydriodic acid, the reduction should fall in the end upon the arsenic, and the arsenious oxide produced should, under proper conditions, preserve the record of the iodine liberated and removed by volatilization. We therefore undertook experimentation upon this line, and the accompanying table shows the results of a preliminary investigation of the mode of action of a mixture of sulphuric and arsenic acids upon an alkaline iodide. In making these tests a standard solution of potassium iodide was put into a test-tube, a solution of potassium arseniate was added, sulphuric acid mixed with its own volume of water was introduced, the volume of the liquid was adjusted, a film of kerosene 3 mm. thick was placed upon the surface of the liquid, and the whole was heated gently and agitated. Kerosene was chosen in preference to other solvents of iodine on account of its lightness, which makes it float upon the mixture, and its high boiling-point, which permits the application of heat to hasten and complete the reaction. Its disadvantage is the persistency with which it adheres to the walls of the test-tube, so that washing with alcohol (or other solvent) after the completion of each test is necessary to prevent the transfer of the iodine of one test to the test next succeeding. The data of these experiments are indicated in the headings.

It will be noted that in Series A, in which the absolute amount of iodine employed, its proportion to the entire volume, and the amount of the arsenic salt remained the same, the proportion of sulphuric acid being the variable element, it is shown that the proportion of sulphuric acid should reach at least twelve parts by volume in one hundred of the solution in order that the maximum distinctness of the test may be developed. An excess of sulphuric acid beyond this proportion is not disadvantageous.

In Series B the proportion and absolute amount of iodine vary as well as the proportion of acid, while the quantity of arsenic remains invariable. The results of this series confirm those of the previous series as to the proper proportion of

sulphuric acid to be used, and the sensitiveness of the test is shown to reach (in round numbers) one part by weight of iodine in six hundred thousand parts of the solution.

KI.	Grms. of Iodine to cm³ of solution.	H_2KAsO_4.	H_2SO_4 [1 : 1].	H_2SO_4 (strong) in 100 parts by volume.	NaCl.	KBr.	Total vol.	Reaction for Iodine.
Series A.								
grm.		grm.	cm³		grm.	grm.	cm³	
0.0001	1 : 132000	1	2	10 : 100	. . .	. .	10	Faint.
0.0001	1 : 132000	1	2	10 : 100	. . .	. .	10	Faint.
0.0001	1 : 132000	1	2.5	12.5 : 100	. . .	. .	10	Faint.
0.0001	1 : 132000	1	2.5	12.5 : 100	. . .	. .	10	Distinct.
0.0001	1 : 132000	1	3	15 : 100	. . .	. .	10	Distinct.
0.0001	1 : 132000	1	4	20 : 100	. . .	. .	10	Distinct.
0.0001	1 : 132000	1	4.5	22.5 : 100	. . .	. .	10	Distinct.
0.0001	1 : 132000	1	5	25 : 100	. . .	1	10	Distinct.
Series B.								
0.0005	1 : 26400	1	2.5	12.5 : 100	. . .	. .	10	Distinct.
0.000133	1 : 99000	1	2.5	12.5 : 100	. . .	. .	10	Distinct.
0.0001	1 : 198000	1	3	10 : 100	0.007	. .	15	Faint.
0.000067	1 : 198000	1	2.5	12.5 : 100	. . .	. .	10	Faint.
0.000067	1 : 198000	1	2.5	12.5 : 100	. . .	1	10	Faint.
0.0001	1 : 198000	1	5	16.6 : 100	0.005	. .	15	Distinct.
0.0001	1 : 198000	1	5	16.6 : 100	0.005	. .	15	Distinct.
0.0001	1 : 264000	1	2.5	6.25 : 100	. . .	. .	20	Invisible.
0.0001	1 : 264000	1	2.5	6.25 : 100	. . .	. .	20	Faint.
0.0001	1 : 264000	1	5	12.5 : 100	. . .	. .	20	Faint.
0.000033	1 : 396000	1	2.5	12.5 : 100	. . .	. .	10	Faint.
0.000033	1 : 396000	1	2.5	12.5 : 100	. . .	. .	10	Faint.
0.000033	1 : 594000	1	5	16.6 : 100	0.005	. .	15	Faint.
Series C.								
0.0020	1 : 8000	1	None. Acetic acid 1.5 grm. (absolute).	. . . . .	. . .	. .	12	Invisible.
0.0010	1 : 13200	. .	5 cm³	25 : 100	. . .	. .	10	Distinct.
0.0002	1 : 66000	. .	5	25 : 100	. . .	. .	10	Faint.
0.0010	1 : 13200	0.2	5	25 : 100	. . .	. .	10	Marked.
0.0001	1 : 132000	0.2	5	25 : 100	. . .	. .	10	Distinct.
0.000033	1 : 198000	0.5	1.25	12.5 : 100	. . .	. .	5	Faint.
0.000033	1 : 198000	0.5	1.25	12.5 : 100	. . .	. .	5	Faint.
0.0001	1 : 264000	2.0	4	10 : 100	. . .	. .	20	Faint.
0.0001	1 : 264000	2.0	6	15 : 100	. . .	. .	20	Faint.

The tests of Series C indicate plainly that it is the sulphuric acid which is the potent agent in liberating the iodine, the

experiment in which acetic acid was substituted for sulphuric acid being particularly noteworthy in this connection. The presence of arsenic acid increases the sensitiveness of the reaction, but its addition beyond a very moderate amount does not appear to be necessary or advantageous. The presence of a chloride or bromide does not impair the delicacy of the test.

The quantities of iodine taken in the experiments just described were necessarily small, and the question arises naturally as to whether the course of action would be similar in the presence of larger amounts of that substance and the correspondingly greater amount of arsenious oxide which is produced with its tendency to reverse the reaction according to which the elimination of iodine proceeds. The solution of this question was reached in the following experiments:

To 50 cm^3 of liquid containing 10 cm^3 of sulphuric acid [1 : 1] and 1 cm^3 of a decinormal solution of iodine in potassium iodide (0.001265 grm. of the former in 0.0018 grm. of the latter) was added 1 cm^3 of a decinormal solution of arsenious oxide (0.00495 grm.), an amount ten times as much as would be necessary to convert the iodine into hydriodic acid were the solution alkaline. The color of the iodine vanished gradually under the action of the arsenious acid, but was restored by the addition of 1 grm. of hydrogen potassium arseniate, and again dispelled by another portion of arsenious acid equal in amount to that introduced at first. Heat was applied at this point, with the result that the color of iodine showed again faintly, and upon boiling the liquid until its volume decreased to 25 cm^3 it became colorless and yielded no iodine when agitated with nitrous acid and chloroform.

An experiment differing from the last in that thirty times as much arsenious oxide and iodine were taken, gave similar results.

It is plain, therefore, that the arsenious acid and arsenic acid exert opposite effects under the conditions of these experiments, and that one or the other prevails according to the proportionate composition of the solution, the degree of dilution, and the temperature.

The experiments detailed in the following statement were intended to determine the conditions best adapted to eliminate the iodine from such quantities of potassium iodide as would ordinarily be dealt with in the course of analysis.

A solution of potassium iodide was placed in an Erlenmeyer beaker of 300 cm^3 capacity, followed by a solution of potassium arseniate and by dilute sulphuric acid [1 : 1], and the volume of the liquid was diluted to about 100 cm^3. A mark was put upon the beaker to indicate the level to which the liquid was to be reduced, a spiral of platinum wire was placed in the solution to prevent explosive ebullition, and the contents of the flask were boiled until the desired degree of condensation was reached. Colorlessness of the liquid at this point, though a fair indication of the absence of free iodine, is no indication that the hydriodic acid has been completely decomposed, and so, in the event of finding the liquid colorless, it was first cooled and shaken with chloroform to prove or disprove the absence of free iodine, and then tested for the presence of hydriodic acid by shaking with nitrous acid and chloroform.

An inspection of these results shows at once that when the larger amounts of iodine are to be eliminated the proportion of sulphuric acid to the final volume after boiling needs to be increased somewhat beyond that which is necessary to set free very small portions such as were dealt with in the experiments of the earlier series.

In Series D it appears that the proportion of sulphuric acid increases from 8.3 per cent to 25 per cent of the whole volume before the liquid is found to be free from iodine as such, and even then there sometimes remain minute though probably insignificant traces of hydriodic acid.

In the experiment of Series E the liquid was diluted after concentration and the boiling repeated, and the volatilization of the iodine was thus more nearly perfected than in the corresponding experiments of the previous series — a proportion amounting to 16.6 per cent apparently accomplishing the work done by 25 per cent of the same acid in a single concentration. The results of Series F, G, and H, are closely comparable with

proportion, and not the absolute amount, of sulphuric acid which is the great factor in the liberation of the iodine. So far as concerns the purposes of good analysis these results indicate the elimination of iodine to a reasonable sufficiency when the reduction of bulk raises the percentage by volume of the strong sulphuric acid to twenty-five and to perfection, as in the latter determinations of Series G, when the percentage reaches twenty-eight and a half. It remains to be seen whether the arsenious oxide reduced in the separation of the iodine will resist successfully, under the conditions of these experiments, the tendency to volatilize which the presence of chlorides and bromides, and the consequent liberation of hydrochloric and hydrobromic acids, might presumably induce.

The experiments of Series I were directed to the elucidation of this point.

Decinormal solutions of iodine and arsenious acid were prepared, standardized, and tested against one another in the usual

SERIES I.

H_2SO_4 [1 : 1].	NaCl.	Final volume.	Per cent of strong H_2SO_4 by volume.	As_2O_3 taken.	As_2O_3 found.	Loss.
cm³	grm.	cm³		grm.	grm.	grm.
10	1	20	25	0.0495	0.0485	0.0010—
10	1	20	25	0.0495	0.0493	0.0002—
10	1	20	25	0.0495	0.0488	0.0007—
10	0.8	20	25	0.0495	0.0488	0.0007—
10	0.5	20	25	0.0495	0.0495	0.0000
20	1	40	25	0.0495	0.0490	0.0005—
20	1	40	25	0.0495	0.0490	0.0005—
20	0.8	40	25	0.0495	0.0490	0.0005—
20	0.5	40	25	0.0495	0.0490	0.0005—
20	0.5	40	25	0.1385	0.1380	0.0005—
20	1	30	33.3	0.0495	0.0476	0.0019—
20	0.8	30	33.3	0.0495	0.0466	0.0029—
20	0.5	30	33.3	0.0495	0.0481	0.0014—
20	0.5	30	33·3	0.0495	0.0485	0.0010—
20	0.5	30	33.3	0.0595	0.0490	0.0005—
20	0.5	30	33.3	0.0495	0.0490	0.0005—
20	0.5	30	33.3	0.0495	0.0490	0.0005—
30	1	60	25	0.0495	0.0485	0.0010—
30	0.8	60	25	0.0495	0.0490	0.0005—
30	0.8	60	25	0.0495	0.0490	0.0005—
30	0.5	60	25	0.0495	0.0490	0.0005—

manner. Definite portions of the solution of arsenious acid were measured from a burette into Erlenmeyer beakers such as were used in the previous experiments, sulphuric acid [1 : 1] and sodium chloride were added, the volume of the liquid was adjusted to 100 cm^3, or a little more, and the process of concentration by boiling was carried to the point desired and indicated by a mark upon the flask. After cooling, the acid was neutralized and the titration effected in the usual manner in the presence of an excess of acid potassium carbonate and starch employed as the indicator. These experiments were arranged upon the presumption that the essential conditions determining the degree of volatility of the arsenic when the reduction is effected by hydriodic acid are imitated, though neither hydriodic acid, nor arsenic acid, nor free iodine is present.

Summary of Series I.

H_2SO_4 [1 : 1].	Final volume.	Per cent of strong H_2SO_4 by volume.	NaCl.	Mean loss of As_2O_3.	Number of determination.
cm^3	cm^3		grm.	grm.	
10	20	25	1	0.0006—	3
20	40			0.0005—	2
30	60			0.0010—	1
10	20	25	0.5 and 0.8	0.0003—	2
20	40			0.0005—	3
30	60			0.0005—	3
20	30	33.3	0.5	0.0008—	5
			0.8	0.0019—	1
			1.0	0.0029—	1

It appears in these results that there is some loss of arsenic in nearly every case within the limits of our experimentation, the amount of volatilization increasing with the ratio of sulphuric acid to the entire volume when the quantity of chloride present is constant, and likewise with the amount of chloride when the ratio of the acid to the total liquid is constant.

The effect of increasing the amount of chloride is naturally accounted for by the "mass action" of the hydrochloric acid thus liberated upon the arsenious oxide in solution; that it is

the proportion, and not the absolute amount, of sulphuric acid which determines the degree of volatility of the arsenic is explicable upon the assumption that the smallest quantity of sulphuric acid employed is sufficient to liberate all the hydrochloric acid (or, at least, nearly all), and that this, by its action on the arsenious oxide, forms the volatile chloride proportionately to the amount of water removed bodily by concentration or withheld from effective action by the attraction of the sulphuric acid.

In extending this line of experimentation to cases involving the action of hydrobromic acid upon arsenious oxide we found it sufficient for our purpose to employ only the highest degree of concentration recorded in the previous experiments and to use 1 grm. of potassium bromide — an amount corresponding, molecule for molecule, to about 0.5 grm. of sodium chloride. The results, given in Series J, indicate that under these circumstances the loss of arsenic is inappreciable.

SERIES J.

H_2SO_4 [1:1].	KBr.	Final volume.	Per cent of strong H_2SO_4 by volume.	As_2O_3 taken.	As_2O_3 found.	Loss.	Mean loss.
cm³	grm.	cm³		grm.	grm.	grm.	grm.
20	1	30	33.3	0.0495	0.0490	0.0005	0.0001—
20	1	30	33.3	0.0495	0.0493	0.0002	
20	1	30	33.3	0.0495	0.0495	0.0000	
20	1	30	33.3	0.0495	0.0495	0.0000	
20	1	30	33.3	0.0495	0.0495	0.0000	

It appears, therefore, from the results of Series I, that, when the amount of sodium chloride present is restricted to 0.5 grm., the liquid may be boiled until the sulphuric acid amounts to 33.3 per cent of it, with a loss, on the average, of 0.0008 grm. of arsenious oxide, and to 25 per cent with a loss of 0.0004 grm. With either of these proportions the results are sufficiently favorable to warrant quantitative testing of a method for separating chlorine and iodine based upon the volatility of iodine and the non-volatility of arsenious oxide under the conditions. The case is even more favorable for the similar separation of

bromine from iodine — the loss of arsenic amounting on the average to 0.0001 grm., under similar conditions. The experiments of Series D to H indicated that the degree of concentration at which all iodine vanishes from the liquid corresponds to the presence of 28.6 per cent of the acid — a point midway between the points of concentration indicated above. We fixed this proportion, therefore, for the following experiments, as being rather more favorable as regards the fixity of the arsenic and perfect as to the elimination of iodine. The smallest absolute amount of sulphuric acid which we have used — 10 cm^3 of the [1 : 1] mixture — demands evaporation of the liquid to a bulk too small to be easily determined with certainty in flasks of the shape and dimensions which we found convenient for this work. The larger amounts of acid are uncomfortably large in the subsequent neutralization. We took, therefore, 20 cm^3 of the [1 : 1] mixture of sulphuric acid and water as the amount best adapted to our purpose and set the limit of concentration at 35 cm^3.

The potassium iodide which we used was prepared with great care, by acting with resublimed iodine upon iron wire, three-fourths of the iodine being added to an excess of iron covered with distilled water, decanting the solution from the excess of iron when the color of iodine had vanished, adding the remainder of the iodine, pouring the filtered solution slowly into boiling water, to which the exact amount of acid potassium carbonate necessary to combine with the iodine had been added, and filtering off the magnetic oxide of iron thus precipitated. The solution of potassium iodide thus made, very faintly alkaline and entirely free from chlorine and bromine, was made up to a suitable volume and standardized by precipitating the iodine of aliquot portions by weight as silver iodide, which was heated and weighed upon asbestos. Weighed portions of this solution, containing approximately 0.5 grm. of potassium iodide to 30 cm^3, were taken for the tests in which the larger quantities of iodine were introduced; measured portions of a solution made by diluting the former were employed in the tests involving the smaller amounts.

The sodium chloride and potassium bromide used were shown to be free from iodine, and the hydrogen potassium arseniate contained no arsenious acid.

The mode of proceeding was, in general, like that of the previous experiments. The solution of potassium iodide was put in an Erlenmeyer beaker of 300 cm³ capacity, two grams of hydrogen potassium arseniate were added in solution and followed by 20 cm³ of sulphuric acid [1 : 1], the liquid was diluted with water to a little more than 100 cm³, a platinum spiral was placed in the flask to secure quiet ebullition, a trap made by cutting off a two-bulb drying tube about an inch from the inside bulb was hung, large end downward, in the mouth of the flask to prevent mechanical loss, and the liquid was boiled until the level reached the 35 cm³ mark put upon the flask. At this point the flask was cooled, the acid nearly neutralized with sodium hydrate in solution, the neutralization completed by acid potassium carbonate, 20 cm³ of the last being added in excess, a definite portion of starch indicator added, and the contents in arsenious acid determined by titration with a decinormal solution of iodine for the larger amounts, and a centinormal solution for the smaller. Due correction was made for the amount of iodine necessary to develop the test-color in a solution prepared and treated similarly in all respects to the experimental solutions excepting the introduction of the iodide — the correction amounting to a single drop more of the decinormal solution than was required to produce the end reaction in the same volume of pure water containing only the starch indicator.

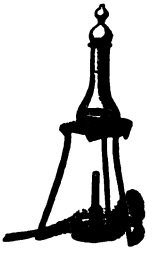


FIG. 1.

The decinormal solution of iodine was made by dissolving 12.65 grms. of carefully resublimed iodine in potassium iodide (proved free from iodate) and diluting to a liter. The centinormal solution was made by diluting the stronger solution. The standardizing was effected by comparison with a solution of arsenious oxide containing 4.95 grm. to the liter. This mode of fixing the value of the solution should and, as the

sequel proved, did indicate the correct standard, but for the sake of confirmation the value of the arsenic solution was redetermined by titration against iodine specially purified by subliming off potassium iodide, resubliming between watch-glasses, and exposing during forty-eight hours over sulphuric acid. Portions of the iodine thus prepared were weighed in a glass-stoppered weighing bottle, dissolved in the same without danger of volatilization by introducing pure solid potassium iodide and a little water, and diluted and treated with the solution of arsenious acid measured from a burette until the color of iodine vanished. The excess of arsenious oxide was determined by titrating against the standard solution of iodine whose value in terms of measured portions of the solution of arsenious oxide was perfectly known.

SERIES K.

H_2SO_4 [1 : 1].	H_2KAsO_4.	NaCl.	KBr.	Final volume.	Iodine corresponding to As_2O_3 reduced.	Chlorine corresponding (average).	Bromine corresponding (average).
cm³	grm.	grm.	grm.	cm³	grm.	grm.	grm.
20	2	0.5	..	35	0.0000		
20	2	0.5	..	35	0.0000	0.0000	....
20	2	0.5	..	35	0.0000		
20	2	..	0.1	35	0.0003		
20	2	..	0.1	35	0.0001	....	0.0001
20	2	..	0.1	35	0.0001		
20	2	..	0.5	35	0.0005		
20	2	..	0.5	35	0.0005	....	0.0003
20	2	..	0.5	35	0.0005		

In Series K are detailed experiments which follow the line marked out for the separation of iodine from chlorine and bromine in the haloid salts, excepting that the iodide was entirely omitted for the purpose of discovering whether hydrochloric and hydrobromic acids possess reducing action upon arsenic acid under the conditions. The evidence is plain that no arsenious oxide is formed by the action of 0.5 grm. of sodium chloride upon 2 grm. of the arseniate under the circumstances as given.

Hydrobromic acid, on the contrary, is slightly decomposed

with the evolution of bromine enough to give visible color to the concentrated liquid, but the amount of bromine lost, as indicated by the arsenious acid produced in its evolution, is only 0.0003 grm. for 0.5 grm. of potassium bromide, and 0.0001 grm. for 0.1 grm. of the bromide. Further experiments indicated, however, that concentration cannot go on to a volume less than 35 cm³ without causing serious loss when the maximum amount of bromide is present.

SERIES L.

No.	H_2SO_4 [1 : 1].	H_3KAsO_4.	NaCl.	KBr.	Final vol.	Theory for Iodine in KI.	Iodine found.	Error.	Average. error.
	cm³	grm.	grm.	grm.	cm³	grm.	grm.	grm.	grm.
(1)	20	2	. .	. .	35	0.4080	0.4079	0.0001—	
(2)	20	2	. .	. .	35	0.4091	0.4086	0.0005—	
(3)	20	2	. .	. .	35	0.4083	0.4086	0.0003+	
(4)	20	2	. .	. .	35	0.0400	0.0396	0.0004—	
(5)	20	2	. .	. .	35	0.0400	0.0391	0.0009—	0.0002—
(6)	20	2	. .	. .	35	0.0400	0.0400	0.0000	
(7)	20	2	. .	. .	35	0.0400	0.0401	0.0001+	
(8)	20	2	. .	. .	35	0.0040	0.0037	0.0003—	
(9)	20	2	. .	. .	35	0.0040	0.0038	0.0002—	
(10)	20	2	0.5	. .	35	0.4077	0.4066	0.0011—	
(11)	20	2	0.5	. .	35	0.4082	0.4073	0.0009—	0.0011—
(12)	20	2	0.5	. .	35	0.4086	0.4073	0.0013—	
(13)	20	2	0.5	. .	35	0.0400	0.0402	0.0002+	
(14)	20	2	0.5	. .	35	0.0400	0.0395	0.0005—	0.0002—
(15)	20	2	0.5	. .	35	0.0040	0.0037	0.0003—	
(16)	20	2	0.5	. .	35	0.0040	0.0037	0.0003—	
(17)	20	2	. .	0.5	35	0.4082	0.4092	0.0010+	
(18)	20	2	. .	0.5	35	0.4138	0.4136	0.0002—	0.0008+
(19)	20	2	. .	0.5	35	0.4083	0.4099	0.0016+	
(20)	20	2	. .	0.5	35	0.0400	0.0410	0.0010+	
(21)	20	2	. .	0.5	35	0.0400	0.0404	0.0004+	0.0008+
(22)	20	2	. .	0.5	35	0.0040	0.0048	0.0008+	
(23)	20	2	. .	0.5	35	0.0040	0.0049	0.0009+	
(24)	20	2	0.5	0.5	35	0.4087	0.4083	0.0004—	
(25)	20	2	0.5	0.5	35	0.4112	0.4111	0.0001—	0.0003—
(26)	20	2	0.5	0.5	35	0.4083	0.4079	0.0004—	

In Series L are given the results of twenty-six determinations of iodine by the method outlined.

Upon inspection of these results it appears that the method is good and reliable under all the conditions tested.

When neither chloride nor bromide is present, the iodine is determinable with a mean error of 0.0002 grm.

When sodium chloride accompanies the iodide, the results show a loss of arsenious oxide and a consequent apparent deficiency of iodine — as we should expect in accordance with the indications of Series I. This deficiency proves to be proportional to the amount of iodide broken up, or the arsenious oxide thus produced. For 0.53 grm., approximately, of potassium iodide and 0.5 grm. of sodium chloride the deficiency measured in iodine amounted to 0.0011 grm. When the potassium iodide is decreased tenfold (or more) the deficiency falls to 0.0002 grm. It should be recalled, too, in this connection that the results of Series I pointed to increasing volatility of the arsenic with the increase of the sodium chloride present.

The presence of potassium bromide results in the liberation of minute amounts of bromine and a consequent increase in the arsenious oxide and apparent excess of iodine. The mean error due to this cause is 0.0008 grm. for 0.5 grm. of the bromide, and the variation in the quantity of iodide present is without effect upon it.

The simultaneous action of the chloride and bromide tends, of course, to neutralize the error due to each. Thus, in the mixture weighing about 1.5 grm. and consisting of sodium chloride, potassium bromide, and potassium iodide in equal parts, the mean error amounts to 0.0003 grm.—. The largest error in the series is 0.0016 grm.+, when the bromide was at its maximum and no chloride was present; and the next largest was 0.0013 grm.—, when the chloride was at its maximum and no bromide was present.

It is obvious that when the amounts of chloride and bromide present are known approximately it is possible to apply corrections which shall eliminate errors in the indicated amount of iodine due to the action of these substances. From the averages of Series L it is apparent that the amount to be added in each case may be obtained by multiplying the product of the weights in grms. of sodium chloride and potassium iodide by the constant 0.004; and the amount to be subtracted, by multiplying the weight in grms. of potassium bromide by 0.0016.

Thus for example, the correction in (24) will be 0.0011 grm. + (= 0.5×0.56×0.004) and 0.0008 grm. − (= 0.5×0.0016). The individual results of Series L thus corrected will stand as follows:

No. of Exp.	Theory for Iodine.	Corrected amount of Iodine found.	Error.	Mean error.
	grm.	grm.	grm.	
(1)	0.4080	0.4079	0.0001−	
(2)	0.4091	0.4086	0.0005−	
(3)	0.4083	0.4086	0.0003+	
(4)	0.0400	0.0396	0.0004−	
(5)	0.0400	0.0391	0.0009−	
(6)	0.0400	0.0400	0.0000	
(7)	0.0400	0.0401	0.0001+	
(8)	0.0040	0.0037	0.0003−	
(9)	0.0040	0.0038	0.0002−	
(10)	0.4077	0.4077	0.0000	
(11)	0.4082	0.4084	0.0002+	
(12)	0.4086	0.4084	0.0002−	
(13)	0.0400	0.0403	0.0003+	0.0001−
(14)	0.0400	0.0396	0.0004−	
(15)	0.0040	0.0037	0.0003−	
(16)	0.0040	0.0037	0.0003−	
(17)	0.4082	0.4084	0.0002+	
(18)	0.4138	0.4128	0.0010−	
(19)	0.4083	0.4191	0.0008+	
(20)	0.0400	0.0402	0.0002+	
(21)	0.0400	0.0396	0.0004−	
(22)	0.0040	0.0040	0.0000	
(23)	0.0040	0.0041	0.0001+	
(24)	0.4087	0.4086	0.0001−	
(25)	0.4112	0.4114	0.0002+	
(26)	0.4083	0.4082	0.0001−	

The mode of proceeding in the analysis of a mixture of alkaline chlorides, bromides, and iodides, according to this method, may be briefly summarized as follows:

The substance (which should not contain of chloride more than an amount corresponding to 0.5 grm. of sodium chloride, nor of bromide more than corresponds to 0.5 grm. of potassium bromide, nor of iodide much more than the equivalent of 0.5 grm. of potassium iodide) is dissolved in water in an Erlenmeyer beaker of 300 cm^3 capacity, and to the solution are added 2 grms. of dihydrogen potassium arseniate dissolved in water, 20 cm^3 of a mixture of sulphuric acid and water in

equal volumes, and enough water to increase the total volume to 100 cm^3, or a little more. A platinum spiral is introduced, a trap made of a straight two-bulb drying-tube cut off short is hung with the larger end downward in the neck of the flask, and the liquid is boiled until the level reaches the mark put upon the flask to indicate a volume of 35 cm^3. Great care should be taken not to press the concentration beyond this point on account of the double danger of losing arsenious chloride and setting up reduction of the arseniate by the bromide. On the other hand, though 35 cm^3 is the ideal volume to be attained, failure to concentrate below 40 cm^3 introduces no appreciable error. The liquid remaining is cooled and nearly neutralized by sodium hydrate (ammonia is not equally good), neutralization is completed by hydrogen potassium carbonate, an excess of 20 cm^3 of the saturated solution of the latter is added, and the arsenious oxide in solution is titrated by standard iodine in the presence of starch.

With ordinary care the method is rapid, reliable and easily executed, and the error is small. In analyses requiring extreme accuracy all but accidental errors may be eliminated from the results by applying the corrections indicated.

II

TWO METHODS FOR THE DIRECT DETERMINATION OF CHLORINE IN MIXTURES OF ALKALINE CHLORIDES AND IODIDES.

By F. A. GOOCH and F. W. MAR.*

THE determination of chlorine associated with iodine in haloid salts is usually accomplished by differential or indirect means: either the two halogens are determined together in a portion of the assay while the iodine alone is estimated in a second portion by one or other of well known methods, the difference between the sum of the halogens and the iodine being the chlorine sought; or, the silver salts of the halogens are weighed together and then converted into a single salt, or the metal, the ratio of chloride to iodide in the original salt being found by simple algebraic processes. If the amounts of iodine involved are minute, it is possible to separate that element by Fresenius's method of treatment with nitrous acid and a solvent like carbon disulphide, and then to determine chlorine directly in the residue; but the manipulation of the process is difficult, and the results inaccurate, when much iodine must be removed. The only method which has been deemed generally applicable to the direct estimation of chlorine associated with iodine in haloid salts is based upon Lassaigne's reaction, by which the iodine is precipitated as palladious iodide; but, the necessity of removing the excess of palladium by hydrogen sulphide before proceeding to precipitate the chlorine is so irksome that, even in this process, it is found to be more convenient to fall back upon the estimation of chlorine as the difference between the iodine found by the palladium process and the sum of the iodine and chlorine

* From Am. Jour. Sci., xxxix, 293.

obtained by another test in another portion of the material. A straightforward and easy method for determining the chlorine is obviously desirable, and in the work of which we here give an account we have endeavored to find such.

It is a well-known fact * that when an aqueous solution of hydrochloric acid is boiled, a point of concentration is reached, by the excessive loss of acid from stronger solutions and of water from weaker ones, at which, for definite barometric pressure, the liquid boils at a constant temperature and distils unchanged in composition. It follows naturally that a degree of dilution may be reached beyond which the loss of the acid must be inappreciable. Indeed, Fleischer justifies his use of hydrochloric acid as a standard in alkalimetric processes upon his observation that decinormal solutions of this acid, and even solutions of twice the strength (7.3 grms. to the litre), do not yield, after ten minutes' boiling, enough acid to redden blue litmus paper held in the steam. Hydriodic acid behaves similarly to hydrochloric acid in the matter of volatilizing from aqueous solutions; but to the decomposing action of oxidizing agents it is far more sensitive. Our endeavor has been to find conditions under which hydriodic acid may be completely broken up, and its iodine removed from the solution by vaporization, while the hydrochloric is retained without appreciable loss. As a first step toward the solution of this question we initiated a series of experiments upon the volatility of hydrochloric acid in solutions containing sulphuric acid, having fixed upon the latter as the most available means of liberating hydrochloric and hydriodic acids from their compounds with the alkaline metals. After a few preliminary experiments with litmus paper exposed in the steam from boiling solutions, we settled down upon two modes of investigating this point. According to the first, the determination of the chlorine remaining after concentration in solutions made up of water, sulphuric acid, and known amounts of the chloride, by precipitating as silver chloride, filtering the precipitate on asbestos, and weighing, was made the test of volatility of the hydro-

* Roscoe and Dittmar, Quart. Jour. Chem., xii, 128.

chloric acid; in the second, the same object was accomplished by estimating the chlorine escaping from the solution, by passing the steam through a condenser and precipitating the acid in the distillate by means of silver nitrate, collecting and weighing the silver chloride as in the former method.

The experiments of Series A to Series F were carried out according to the first method. In them portions of a dilute solution of potassium chloride of known value were measured from a burette into Erlenmeyer flasks of 500 cm^3 capacity, sulphuric acid diluted one-half was added, and the solution was boiled until the flask and contents removed from the flame and placed upon counterpoised scales just tipped the beam. A few trials sufficed to bring the weight to the required point, and the degree of concentration was determined by this means far more accurately than by lowering the level of the liquid to marks placed upon the flasks. The hydrochloric acid remaining after concentration was determined as described, the comparison of the result with the value of the standard solution of chloride indicating, of course, the total loss in the process.

In the experiments of Series A, B, C, D, the effect is traced of increasing proportions of chloride as compared with the same amount of sulphuric acid taken. In those of Series C, E, F, the influence of changing proportions of sulphuric acid, while the amount of chloride remains the same, is brought out. In both sets the evidence is plain that the volatility of the hydrochloric acid is dependent upon the proportion of sulphuric acid as well as upon the amount of the chloride present. It appears likewise that when the amounts of sulphuric acid present are reasonably small the loss of hydrochloric acid is inconsiderable, if the concentration is not pushed to too great an extreme.

The quantities of chloride dealt with in the preceding experiments are rather smaller than those which would naturally be handled in practical analysis, so that it seemed best to extend the experimentation to solutions of greater dilution and containing larger amounts of chloride. In the experiments of Series G, and subsequently, the second mode of treatment

referred to was adopted. The flask was filled as before, but was connected with an ordinary glass condenser so that the distillate might be collected and measured, and the hydrochloric acid condensed with the steam was estimated by pre-

Taken H_2SO_4 [1 : 1].	Taken KCl = HCl		Found AgCl = HCl.		Initial volume.	Final volume.	Error.
cm³	grm.	grm.	grm.	grm.	cm³	cm³	grm.
Series A.							
10	0.05	0.0245	0.0963	0.0245	110	65	0.0000
10	0.05	0.0245	0.0957	0.0243	110	45	0.0002—
10	0.05	0.0245	0.0945	0.0240	110	40	0.0005—
10	0.05	0.0245	0.0941	0.0239	110	35	0.0006—
10	0.05	0.0245	0.0871	0.0221	110	30	0.0024—
10	0.05	0.0245	0.0821	0.0209	110	25	0.0036—
Series B.							
10	0.1	0.0489	0.1910	0.0485	110	65	0.0004—
10	0.1	0.0489	0.1922	0.0488	110	55	0.0001—
10	0.1	0.0489	0.1908	0.0485	110	45	0.0004—
10	0.1	0.0489	0.1894	0.0482	110	35	0.0007—
Series C.							
10	0.2	0.0978	0.3887	0.0976	110	75	0.0002—
10	0.2	0.0978	0.3838	0.0976	110	65	0.0002—
10	0.2	0.0978	0.3831	0.0974	110	55	0.0004—
10	0.2	0.0978	0.3816	0.0970	110	45	0.0008—
10	0.2	0.0978	0.3746	0.0953	110	35	0.0025—
10	0.2	0.0978	0.3322	0.0845	110	25	0.0133—
Series D.							
10	0.4	0.1956	0.7690	0.1955	110	60	0.0001—
10	0.4	0.1956	0.7682	0.1954	110	50	0.0002—
10	0.4	0.1956	0.7574	0.1926	110	35	0.0030—
Series E.							
5	0.2	0.0978	0.3845	0.0978	105	55	0.0000—
5	0.2	0.0978	0.3838	0.0976	105	45	0 0002—
5	0.2	0.0978	0.3823	0.0972	105	35	0.0006—
5	0.2	0.0978	0.3788	0.0963	105	25	0.0015—
Series F.							
20	0.2	0.0978	0.3782	0.0962	120	75	0.0016—
20	0.2	0.0978	0.3602	0.0916	120	65	0.0062—
20	0.2	0.0978	0.3087	0.0785	120	55	0.0193—
20	0.1	0.0978	0.2931	0.0745	120	45	0.0233—

cipitation as silver chloride, the last being dried and weighed as such upon asbestos. The details of the experiments are given in the tabular statement.

SERIES G.

Taken H_2SO_4 [1 : 1].	Taken KCl = HCl		Initial volume.	Final volume.	Time in minutes.	Found AgCl.	Loss of HCl.
cm^3	grm.	grm.	cm^3	cm^3		grm.	grm.
10	1	0.4888	400	300	29	0.0005	0.0001
10	1	0.4888	400	300	22	0.0008	0.0002
10	1	0.4888	350	300	10	0.0004	0.0001
10	1	0.4888	350	300	9	0.0005	0.0001
10	1	0.4888	300	200	25	0.0008	0.0002
10	1	0.4888	200	100	27	0.0021	0.0005
10	1	0.4888	100	50	20	0.0037	0.0009

It is obvious from these results that a solution containing 10 cm^3 of the 1 : 1 sulphuric acid, or 5 cm^3 of the strong acid, may be concentrated to 200 cm^3 without significant loss of hydrochloric acid. At a concentration of 100 cm^3 the loss is notable. In later experiments, we found that a small part of the precipitate which we weighed in these experiments must in reality have resulted from the action of the solution upon the rubber stopper and connectors of the apparatus; for the distillate from pure water in the same apparatus yielded a precipitate, probably silver sulphide, which, filtered off and weighed, was found to amount to 0.0003 grm. The figures of Series G, therefore, overstate somewhat the volatility of hydrochloric acid under the circumstances, but the misrepresentation is inconsiderable. We fixed upon 300 cm^3 as a convenient volume of liquid to manipulate in future experiments, and one sufficiently dilute to guarantee security against the volatilization of hydrochloric acid when the amount of sulphuric acid does not exceed 5 cm^3 of the strong acid, and when the quantity of potassium chloride present does not exceed 1 grm.

The next point to be considered was the proper mode of breaking up hydriodic acid and volatilizing the iodine thus set free, while leaving the hydrochloric acid fixed.

The use of dihydrogen potassium arseniate, which has been utilized to liberate iodine according to a method recently developed in this laboratory,* is precluded by the necessarily high degree of dilution of the solution employed. The first trials were made, therefore, with ferric alum to act as the oxidizing agent according to the well known reaction of Duflos:

$$2H\text{-}I + Fe_2(SO_4)_3 = 2FeSO_4 + H_2SO_4 + I\text{-}I$$

We found by experiment that from a volume of 300 cm^3 containing 10 cm^3 of sulphuric acid [1 : 1], 5 grms. of ferric alum, and 0.005 grm. of potassic iodide, every trace of iodine had disappeared so completely after five minutes' boiling that nitrous acid and chloroform collected no color in the cooled liquid. It transpired, however, that when the amount of potassium iodide was increased to 1 grm., iodine was found in considerable amount after boiling for an hour with occasional replacing of the water evaporated, so that the volume should not decrease much below 300 cm^3. The failure of the iron alum to expel the iodine is not attributable to a deficiency in amount; for the 5 grm. present were capable of decomposing more than a gram and a half of potassium iodide were the full effect theoretically possible attained. Furthermore, special tests in which the amount of ferric alum was increased developed the fact that the increase was but little helpful. The apparent explanation of the phenomenon is that here, as in the liberation of iodine by means of dihydrogen potassium arseniate, there occurs a time in the course of action when for a given degree of dilution an equilibrium is established between the tendency of the oxidizer to oxidize and that of the reduced residue to reverse the action. The obvious modes of securing completed action are the concentrating of the liquid and the reinforcing of the oxidizer. Application of the former is precluded by the danger of volatilizing hydrochloric acid; the simplest mode of realizing the latter — and as the result proved, a feasible one — is the reoxidation of the reduced ferrous sulphate by means of nitric acid.

* Gooch and Browning, Am. Jour. Sci. xxxix, 188. This volume, p. 1.

When a sufficient amount of nitric acid is added to restore the iron to the ferric state, the boiling of the solution resulted in the complete liberation of the iodine. In dilute solutions the amount of nitric acid necessary to oxidize a fixed quantity of ferrous salt is greater than in concentrated solutions. Thus, while 0.1 cm^3 of strong nitric acid should be more than enough to reoxidize the iron reduced by 1 grm. of potassium iodide when the full oxidizing action is brought out, we found it necessary to add to the dilute solutions with which we worked about 2 cm^3 of the acid to complete the action satisfactorily. Incidentally, we found that the nitric acid by itself — that is, without the presence of the iron salt — is not effective in liberating the iodine; for, the successive addition of portions of 1 cm^3 of nitric acid to a solution containing 10 cm^3 of sulphuric acid [1 : 1], and 1 grm. of potassium iodide in a total volume of 400 cm^3 until the amount of nitric acid reached 5 cm^3, the liquid boiling all the time, liberated but little iodine, while the addition at this point of 2.5 grm. of ferric alum determined the evolution of iodine in dense fumes.

The addition of 2 cm^3, or at the most 3 cm^3, of strong nitric acid to solutions constituted as has been described proved to be sufficient to liberate the entire amount of iodine present. The question as to whether the hydrochloric acid is affected by the addition of so much nitric acid was settled in the experiments of the following series. In these determinations a little sulphurous acid was added to each distillate to insure the complete precipitation of the chlorine by silver nitrate, and sufficient nitric acid was added to redissolve the silver sulphite thrown down also at first.

It appears in these results that the ferric salt has no perceptible influence upon the hydrochloric acid, and that the presence of nitric acid within reasonable limits does not sensibly increase the loss of hydrochloric acid which takes place under conditions otherwise similar, strong nitric acid to the amount of 5 cm^3 in a total volume of 300 cm^3 producing no apparent increment of loss from half a gram of hydrochloric

the whole volume was brought to 400 cm³, and the liquid was boiled with the addition of nitric acid as indicated in the table, 1 cm³ being added after it appeared that all iodine had been expelled.

The color of the ferric salt renders it impossible to tell by the appearance of the solution the exact moment when the iodine has been expelled, and starch paper loses its sensitiveness in hot vapors. We bestowed some attention, therefore, upon means for the detection of small amounts of iodine in hot steam in order to avoid the inconvenience of condensing the distillate and testing it for iodine. We found that red

SERIES I.

H_2SO_4 [1 : 1].	$Fe_2(SO_4)_3$.	HNO_3.	KCl = HCl.		KI.	Initial volume.	Final volume.	Time in minutes.	AgCl = HCl found.		Error.
cm³	grm.	cm³	grm.	grm.	grm.	cm³	cm³		grm.	grm.	grm.
10	2*	. .	0.4960	0.2425	. .	400	300	40	0.9536	0.2425	0.0000
10	2*	. .	0.4970	0.2429	. .	400	300	40	0.9534	0.2624	0.0005−
10	2*	. .	0.4942	0.2416	. .	400	300	30	0.9509	0.2418	0.0002+
10	2*	2	0.4969	0.2429	. .	400	300	30	0.9559	0.2431	0.0002+
10	2*	3	0.4956	0.2423	1	400	350	30	0.9546	0.2428	0.0005+
10	2*	3	0.4969	0.2429	1	400	350	23	0.9662	0.2432	0.0003+
10	2†	3	0.4949	0.2419	1	400	300	27	0.9523	0.2422	0.0003+
10	2†	5	0.4970	0.2429	1	400	250	55	0.9559	0.2431	0.0002+
10	2†	5	0.4955	0.2422	1	400	300	30	0.9524	0.2422	0.0000
10	2†	5	0.4967	0.2428	1	400	300	33	0.9546	0.2428	0.0000
10	2†	6	0.4964	0.2427	1	400	300	30	0.9550	0.2429	0.0002+

litmus, preferably wet, is a most sensitive agent for the detection of iodine under the circumstances, taking on with exposure to traces of the vapor carrying that element, a distinct gray-blue, deepening with exposure to larger amounts into a lavender-blue. The addition of 0.005 grm. of iodine to 400 cm³ of boiling water produces immediately upon red litmus paper the characteristic lavender-blue color, and the test grows fainter and fainter as fresh test-papers are exposed, until at the end of five minutes, or thereabouts, when the litmus paper shows no color, the cooled solution yields no

* The iron was added in the form of iron alum.

† The iron was added as $FeSO_4$ oxidized by HNO_3.

iodine to nitrous acid and chloroform. This reaction of litmus we found of great value and in no case in which an exposure of two minutes' duration failed to develop the characteristic color were we able to find iodine in the cooled liquid. To prevent mechanical loss of liquid we made use of the trap described in a previous paper from this laboratory, consisting simply of an ordinary two-bulb straight drying tube cut off short and hung with the large end downward in the mouth of the Erlenmeyer flask.* The residue in the flask after the expulsion of the iodine was treated with silver nitrate, and the precipitated chloride was determined similarly to that obtained in standardizing the solution of potassium chloride.

Several determinations in blank — that is, experiments from which the iodine was purposely omitted — are included, for the sake of comparison, in the tabular statement.

These eminently satisfactory results prove the trustworthiness of the method.

The fact that nitric acid appears to affect so little the hydrochloric acid in the solution, suggested the possibility that nitrous acid itself might be turned to account and used in a similar process instead of a ferric salt and nitric acid. Some preliminary experiments were made, therefore, to test the behavior of hydrochloric acid under the action of nitrous acid, and, as they gave favorable indications, the experiments of Series J were undertaken to test the action quantitatively. The general conduct of the test was similar to that followed in Series I. The solution of chloride and iodide containing 10 cm^3 of sulphuric acid [1 : 1] was diluted to 400 cm^3, and agitated while the gas developed by the action of sulphuric acid on 2 grm. of sodium nitrite was passed into it. With pure sodium nitrite at hand there is probably no serious objection to introducing that substance directly into the solution, but impurities in the article at our disposal made it desirable to generate the gas outside the solution.

For a generator we used two straight drying tubes con-

* See figure p. 12.

nected by a rubber tube and set up after the fashion of the von Babo generator, and regulated the rapidity of the current to a rate of five or six bubbles to the second by changing the relative elevation of the generator tubes. The iodine separates immediately upon the introduction of the nitrous fumes and escapes upon boiling in dense fumes, leaving the solution colorless in a very short time. The litmus test was applied as an additional safeguard to indicate the completion of the removal of the iodine. The results of the experiments as given in the accompanying table are evidently satisfactory.

SERIES J.

H_2SO_4 [1 : 1.]	$NaNO_2$ used in generator.	KCl = HCl.		KI.	Initial volume.	Final volume.	Time in minutes.	AgCl = HCl found.	found.	Error.
cm^3	grm.	grm.	grm.	grm.	cm^3	cm^3		grm.	grm.	grm.
10	2	0.4953	0.2421	1	400	350	20	0.9524	0.2422	0.0001+
10	2	0.4975	0.2432	1	400	350	16	0.9573	0.2434	0.0002+
10	2	0.4956	0.2423	1	300	250	15	0.9530	0.2423	0.0000
10	2	0.4973	0.2431	1	300	250	15	0.9550	0.2429	0.0002−
10	2	0.4964	0.2427	1	300	250	15	0.9550	0.2429	0.0002+
10	2	0.4969	0.2429	1	300	250	15	0.9567	0.2433	0.0004+

The modes of proceeding to the separation of iodine and the estimation of chlorine according to the processes which we have detailed may be briefly summarized as follows:

First Method. — To the solution of the alkaline chloride and iodide diluted to about 400 cm^3 in an Erlenmeyer flask capable of containing a liter, are added 10 cm^3 of sulphuric acid of half strength, with 2 grm. of ferric sulphate (either in the form of iron alum, or ferrous sulphate oxidized in concentrated solution by about 0.3 cm^3 of nitric acid), and 3 cm^3 of nitric acid. A trap, of the form described, is hung in the neck of the flask, and the liquid is boiled until the steam which escapes no longer gives to red litmus paper, after two minutes' exposure, the characteristic gray-blue due to traces of iodine. Then 1 cm^3 more of nitric acid is added, and the test for iodine again made. When no iodine is found in the

escaping vapor, silver nitrate is added in excess to the contents of the flask, the precipitate is settled, collected in a perforated crucible on asbestos, dried, and weighed as silver chloride.

Second Method. — The solution of the chloride and iodide contained in an Erlenmeyer flask is diluted to 400 cm^3; 10 cm^3 of sulphuric acid of half strength are added, and the vapor from 2 grm. of sodium nitrite acted upon by dilute sulphuric acid (preferably in a simple generator, such as is described above) is passed with reasonable rapidity into the agitated solution. The liquid is boiled until colorless, and still further until litmus paper placed in the steam gives no reaction for iodine after an exposure of two minutes. The contents of the flask are treated with silver nitrate, and the precipitated chloride is treated exactly as in the first method.

Both methods are convenient and precise.

III

A METHOD FOR THE REDUCTION OF ARSENIC ACID IN ANALYSIS.

By F. A. GOOCH and P. E. BROWNING.*

HOLTHOFF'S development of Mohr's suggestion relative to the reduction of arsenic acid to the lower condition of oxidation by the action of sulphurous acid, † with the demonstration that arsenic acid can be evaporated even to dryness in presence of hydrochloric acid without danger of significant volatilization, has placed the analysis of ordinary compounds of arsenic, both natural and artificial, within the scope of Mohr's classical and exact method of determination by titration with iodine. As Holthoff left the method, it is satisfactory, so far as regards accuracy, and as modified by McCay, ‡ who substitutes for the four hours' digestion heating for one hour in a pressure-bottle, is eminently successful. In the account of the experiments about to be described we detail our experience in an attempt to shorten still further the process of reduction of arsenic acid by making use of hydriodic acid as the active agent instead of sulphurous acid.

In a recent paper § we have described a method for the determination of iodine in haloid salts based upon the action of arsenic acid, in the presence of sulphuric acid, according to the equation,

$$H_3AsO_4 + 2H\text{-}I = H_3AsO_3 + H_2O + I\text{-}I,$$

the iodine being completely volatilized, but leaving behind in the arsenious acid produced by the action the record of the

* From Am. Jour. Sci., xl, 66.

† Zeitschr. anal. Chem., xxiii, 378.

‡ Am. Chem. Jour., vii, 373.

§ Am. Jour. Sci., xxxix, 188. This volume, p. 1.

amount of hydriodic acid orginally present. This reaction we propose to utilize conversely, and to employ potassium iodide in excess, in presence of sulphuric acid, to bring about the reduction of the arsenic acid to arsenious acid which may be determined, after neutralization, by the iodine method. The conditions of the methods are different in that in the former the hydriodic acid is entirely broken up by the action of the arsenic acid, and the iodine volatilizes easily, while in the latter some hydriodic acid must remain in solution until a very low degree of concentration is reached, and remaining must exhibit its characteristic proneness to retain free iodine.

We find in practice that when a solution made up to contain sulphuric acid, an arseniate and potassium iodide to an amount somewhat in excess of that theoretically demanded to effect the conversion of the arsenic acid to arsenious acid, is boiled, iodine is evolved and the color of the liquid passes from the dark red when the iodine is abundant through the various gradations of tint to a canary yellow, and then, as the sulphuric acid reaches a degree of concentration sufficient to determine by its own specific action the liberation of iodine, the color again darkens, and if the process of concentration is continued, and much arsenic is present, crystals of arsenious iodide separate and form more abundantly on cooling. If evaporation is pushed still farther the arsenious iodide begins to volatilize and at the point where the sulphuric acid fumes the liquid loses all color and the arsenic has vanished more or less completely. In one experiment conducted in this manner it was found, by the method to be described later, that of 0.3861 grm. of arsenic pentoxide originally present with 1 grm. of potassium iodide and 10 cm^3 of sulphuric acid [1 : 1] the equivalent of 0.1524 grm. remained. In another similar experiment in which, however, only a few milligrams of arsenic oxide were involved not a trace of arsenic remained at the end.

It is obvious that two points in this course of action demand examination at the outset. First, means must be found for removing the remnant of free iodine which is withheld by the

hydriodic acid, or of rendering it harmless in the titration process to follow; and, secondly, the degree to which the solution may be concentrated without loss of arsenic must be fixed. In our work upon the converse of this process, we noted particularly the marked influence of the amount of sulphuric acid present upon the degree of concentration necessary to expel the iodine. We turned attention, therefore, at once to this point in the present case and investigated the effect of varying the proportion of sulphuric acid in solutions containing definite amounts of potassium iodide and potassium arseniate. The volume of the solution was made up to about 100 cm^3 and concentrated by boiling until the color was faintest. Then to determine provisionally, and for preliminary purposes, the point at which volatilization of arsenic was likely to occur, the concentration was continued until the arsenious iodide began to separate. The results are tabulated as follows:

KI.	As_2O_5.	H_2SO_4 [1 : 1].	Volume when color was lightest.	Volume when AsI_3 appeared.
grm.	grm.	cm^3	cm^3	cm^3
1	0.1900	20	80	33
1	0.1900	15	65	25
1	0.1900	10	40	19
1	0.1900	5	30	11

The amount of sulphuric acid which, considering rapidity in concentrating to the proper point, ease in neutralizing the acid previous to titration, and general convenience in manipulation, seemed to be best was 10 cm^3 of the mixture made by diluting the acid with an equal volume of water. This we fixed upon for use in future experiments and set the limit of concentration at 40 cm^3.

It is manifest from the phenomena described that when much hydriodic acid remains in the solution the last portions of free iodine cannot be completely removed by heat without volatilization of the arsenic. We experimented, therefore, upon the effect of very dilute sulphurous acid upon the remnant of iodine in liquids constituted as described and concentrated to

40 cm³, the point of minimum color, the solution of sulphurous acid which we employed corresponding approximately to centinormal iodine. We found that upon adding the sulphurous acid drop by drop to the hot concentrated solution the point at which the color vanished could be determined without difficulty, but that if the solution was permitted to stand a single minute the color of iodine returned, doubtless developed by the action of air upon the hot hydriodic acid. We adopted, therefore, the plan of at once diluting the solution with cold water as soon as the sulphurous acid had done its work and immediately neutralizing with potassium carbonate. When this mode of proceeding was followed we were unable to find evidence of reversion of arsenious acid to arsenic acid, magnesia mixture producing in the solution no precipitate of the ammonium magnesium arseniate.

Following out the same general lines, therefore, we proceeded to the quantitative examination of the process. Portions of a standard solution of the dihydrogen potassium arseniate were measured from a burette into counterpoised Erlenmeyer flasks of 250 cm³ capacity, and the increase in weight was taken as the measure of the actual amount of the solution employed. Potassium iodide in solution, and 10 cm³ of sulphuric acid [1:1] were added, and the liquid was diluted with water to a volume of about 100 cm³. A trap made, as described in our paper upon the reverse of this process, by cutting down a two-bulbed drying tube,* was hung in the neck of the flask to prevent mechanical loss, and the liquid was rapidly concentrated by boiling until the volume of 40 cm³, the point at which the color of iodine had faded to a pale yellow, was reached. At this point the flask was removed from the flame, its sides and the trap were quickly washed down, the weak sulphurous acid was added drop by drop from a burette until the color of the free iodine had just vanished, the liquid was immediately diluted with cold water, the free acid was nearly neutralized with potassium carbonate and the point of neutralization was reached and passed a little by the addition of the acid potassium

* See figure on p. 12.

carbonate. After cooling completely, a definite amount of starch solution was added and the titration of the arsenious acid was proceeded with as usual, due correction being made for the amount of iodine necessary to produce the end color into the volume of liquid and starch solution employed.

The value of the standard solution of the arseniate was fixed by two series of determinations. One series was made according to Levol's method of precipitating the ammonium magnesium arseniate and weighing as the pyroarseniate, modified, however, in that the precipitate was collected on asbestos in a perforated crucible and ignited after moistening with ammonium nitrate. In the second series McCay's modification* of Reich's method was followed, excepting that the silver arseniate was collected, dried and weighed on asbestos in a perforated crucible. The mean of several closely agreeing determinations gave the contents of 50 grms. of the solution in arsenic pentoxide as 0.3824 grm. by Levol's method and 0.3830 grm. by McCay's modification of Reich's process. We took the mean of these figures, 0.3827 grm., as the standard of the solution.

The details of the experiments with this solution are recorded in the following table.

KI taken.	H_2SO_4 [1 : 1]. taken.	As_2O_5 taken.	As_2O_5 found.	Error.
grm.	cm^3	grm.	grm.	grm.
1.5	10	0.3861	0.3862	0.0001+
1.5	10	0.3862	0.3856	0.0006—
1.5	10	0.3861	0.3862	0.0001+
1.5	10	0.3860	0.3862	0.0002+
1.5	10	0.3863	0.3862	0.0001—
1.5	10	0.3862	0.3862	0.0000
1	10	0.1927	0.1922	0.0005—
1	10	0.1928	0.1922	0.0006—
1	10	0.1930	0.1925	0.0005—
1	10	0.1930	0.1927	0.0003—
1	10	0.1936	0.1929	0.0007—
1	10	0.1929	0.1928	0.0001—

Experiments in which smaller quantities of arsenic were handled were made similarly, excepting that the standard

* Am. Chem. Jour., viii, 77.

solution, from which portions for the tests were measured, was made by diluting the former standard ten times, and centinormal iodine was used in the titration.

KI taken.	H_2SO_4 [1 : 1] taken.	As_2O_5 taken.	As_2O_5 found.	Error.
grm.	cm³	grm.	grm.	grm.
1	10	0.0383	0.0380	0.0003—
1	10	0.0383	0.0385	0.0002+
0.5	10	0.0383	0.0384	0.0001+
0.4	10	0.0383	0.0385	0.0002+
0.3	10	0.0383	0.0386	0.0003+
0.2	10	0.0383	0.0384	0.0001+
0.2	10	0.0076	0.0074	0.0002—
0.2	10	0.0076	0.0074	0.0002—
0.2	10	0.0038	0.0034	0.0004—
0.2	10	0.0038	0.0034	0.0004—

When the amount of hydriodic acid in solution is small, correspondingly small amounts of iodine are retained after concentration. In the following experiments colorless solutions were obtained and, for the sake of comparison with the previous results, these solutions were neutralized and titrated without treatment with sulphurous acid, there being no apparent need for adding it in these cases.

KI taken.	H_2SO_4 [1 : 1] taken.	As_2O_5 taken.	As_2O_5 found.	Error.
grm.	cm³	grm.	grm.	grm.
0.2	10	0.0038	0.0035	0.0003—
0.2	10	0.0038	0.0035	0.0003—

It appears, therefore, that the average error of the whole number of determinations (twenty-four) made by this process amounts to rather less than 0.0002 grm. —, falling between extremes of 0.0003 grm. + and 0.0007 grm. —. The entire amount of arsenic pentoxide handled in the twenty-four determinations was 3.7351 grms., and of this 3.7309 grm. were indicated in the titration as reduced to the arsenious condition. The loss 0.0042 grm. — the entire error of the process — amounts to 0.11 per cent of the amount taken.

Certain experiments were made to see whether the period of evaporation might not be dispensed with by so modifying the process that the entire amount of iodine set free in the action of the sulphuric acid, the arseniate, and the iodide might be reconverted at once by sulphurous acid to the condition of hydriodic acid. The conversion was apparently successful, but the results of the modification were several per cent below the truth, indicating that the digestion during evaporation, or the removal of the free iodine, or the combined effect of the two, is essential to the completion of the reduction of the arsenic.

The process as we recommend it may be summarized briefly as follows: — To the arseniate in solution are to be added potassium iodide in excess of the amount needed according to the equation to complete the reduction, and 10 cm^3 of half and half sulphuric acid. The liquid is to be diluted to about 100 cm^3 and boiled rapidly (with the precautions of trapping as described) until the volume is decreased to 40 cm^3. The color of free iodine is to be bleached by cautious additions of sulphurous acid (corresponding roughly to centinormal iodine) and instantly diluted with water and neutralized with potassium carbonate, the neutral carbonate at the first and afterward the acid carbonate. The whole is to be cooled and titrated as usual with iodine, using starch as an indicator. Its advantage is in the rapidity with which it may be executed, the whole operation being easily completed in a half-hour.

IV

THE DIRECT DETERMINATION OF BROMINE IN MIXTURES OF ALKALINE BROMIDES AND IODIDES.

By F. A. GOOCH and J. R. ENSIGN.*

In a recent paper from this laboratory † two methods were elaborated for the direct determination of chlorine in mixtures of alkaline chlorides and iodides. These methods are based upon the action of oxidizing agents in presence of free sulphuric acid, upon dilute solutions of the haloid salts at the boiling temperature. Under conditions properly controlled, iodine is entirely eliminated by volatilization, leaving the chlorine combined and undisturbed. In the work of which this paper is an account we have endeavored to determine the applicability of the same reactions to the separation of bromine from iodine in similar association. It appeared very early in the work that the exact conditions which were found suitable in the separation of chlorine and iodine are inappropriate to the separation of bromine and iodine. Thus, while according to one of the two methods which we discuss, the gas evolved from 2 grms. of sodium nitrite, passed into a solution containing in 400 cm^3 0.5 grm. of potassium chloride, 1 grm. of potassium iodide, and 5 cm^3 of strong sulphuric acid, eliminated the iodine with a mean error of 0.0002 grm. +, and, while according to the other process the iodine was removed by the action of 2 grms. of ferric sulphate and 3 cm^3 of nitric acid upon a solution similarly constituted otherwise with a mean error of 0.0001 grm., it was found that like con-

* From Am. Jour. Sci., xl, 145.

† Gooch and Mar, Am. Jour. Sci., xxxix, 293. This volume, p. 18.

ditions in certain experiments in which potassium bromide replaced the chloride were productive of errors amounting to from 0.0100 grm. to 0.0200 grm. in both processes. It was evident, therefore, that the reactions which obtained in these processes must be carefully studied and adjusted to make them applicable to the separation of bromine and iodine. Attention was turned at the outset to the behavior of the bromide taken by itself — that is, unaccompanied by an iodide — in boiling solutions containing the reagents of the process. Measured portions of solutions of potassium bromide and of the other reagents were brought to definite volume and boiled in a distillation flask connected with a condenser. The measured distillate was treated with silver nitrate after the addition of a few drops of sulphurous acid to convert free bromine to hydrobromic acid, and, after the addition of an excess of nitric acid to dissolve precipitated sulphite the silver bromide was settled, filtered off upon asbestos in a perforated crucible, dried and weighed. The details of these experiments are given in the accompanying tabular statement.

H_2SO_4 [1 : 1].	HNO_3.	KBr taken.	= HBr.	Initial volume.	Final volume.	AgBr found in the distillate.	= HBr lost.
			I.				
cm³	cm³	grm.	grm.	cm³	cm³	grm.	grm.
10	. .	1	0.6799	400	300	0.0001	trace
10	. .	1	0.6799	300	200	0.0003	0.0001
10	. .	1	0.6799	200	100	0.0006	0.0003
10	. .	1	0.6799	100	50	0.0024	0.0010
10	. .	1	0.6799	50	25	0.0196	0.0084
			II.				
. .	3	1	0.6799	600	500	0.0002	0.0001
. .	3	1	0.6799	500	400	0.0001	trace
. .	3	1	0.6799	400	300	0.0002	0.0001
. .	3	1	0.6799	300	200	0.0004	0.0002
. .	3	1	0.6799	200	100	0.0019	0.0008
. .	3	1	0.6799	100	50	0.0224	0.0096

From the experiments of Series I, it becomes plain that 5 cm^3 of strong sulphuric acid (added as 10 cm^3 of the mixture made by diluting the strong acid with an equal volume of water) and 1 grm. of potassium bromide do not interact in a way to set bromine free or to volatilize hydrobromic acid appreciably until the volume of the liquid has decreased by boiling to about 100 cm^3. The results of Series II show, in like manner, that the effect of 3 cm^3 of nitric acid — the amount which was found to be suitable in the separation of iodine and chlorine in presence of a ferric salt — is not significant until the liquid is concentrated to 200 cm^3. The combined effect of the two acids, as shown in the experiment of Series III, is somewhat different. Here it is evident that bromine is liberated at the highest degree of dilution employed, though the loss is hardly significant in a volume of liquid larger than 400 cm^3. In the experiments of Series IV, the effect of increasing the proportions of nitric acid, while keeping the amount of sulphuric acid and the degree of change in dilution constant, was manifestly to magnify the decomposition of the hydrobromic acid.

In Series V to VIII, hydrobromic acid was employed instead of the bromide. From the results of series V, it becomes evident that concentration of the pure hydrobromic acid may be pressed to 15 cm^3 without incurring serious loss. The effect of the presence of sulphuric acid in raising the limit below which the volatilization of hydrobromic acid begins appreciably, is plain in the figures of Series VI. Series VII sets the volume of 400 cm^3 as the limit to which the same amount of hydrobromic acid may be concentrated without loss in presence of 5 cm^3 of nitric acid. Series VIII indicates unmistakably that even at a volume of 500 cm^3 the combined influences of sulphuric acid, nitric acid and ferric sulphate, taken in the amounts named, remove bromine, the loss being greater when the sulphuric acid is present than is the case when the nitric acid and ferric sulphate are present without it.

The general indication of all these results taken together and brought into comparison would seem to be that improve-

ment in the processes for separating iodine by the use of the reagents whose action is here studied should lie in the direction of greater dilution of the solution treated. Accordingly certain experiments were undertaken following the same general plan already laid down, excepting that the original volume of the liquid boiled was taken much larger than before, and the concentration guarded. Determinations were first made in blank; — that is to say, the process was completed in all respects as if iodine were present and to be separated, exceping that no iodide was introduced. To the solution of the bromide, weighed in an Erlenmeyer flask of 1200 cm^3 capacity, were added 10 cm^3 of sulphuric acid [1 : 1], and either 2 grm. of ferric sulphate and 5 cm^3 of nitric acid were introduced or, after diluting to at least 600 cm^3 of water, the gas from 2 grms. of sodium nitrite was passed into the liquid, the trap, consisting of an abbreviated calcium chloride tube with two bulbs, was hung in the neck of the flask,* and the boiling was continued for at least an hour and a half. Finally the solution was cooled, treated with silver nitrate, and the silver bromide precipitated was settled, filtered off on asbestos in a perforated crucible, dried and weighed. The details of treatment are given in the table.

TABLE IX.

H_2SO_4 [1 : 1].	$NaNO_2$ used in generator.		KBr = HBr taken.		Initial volume.	Final volume.	Time in minutes.	AgBr = HBr found.		Error in HBr.
cm^3	grm.		grm.	grm.	cm^3	cm^3		grm.	grm.	grm.
10	2		0.5394	0.3667	800	500	120	0.8506	0.3665	0.0002
10	2		0.5387	0.3663	700	400	90	0.8492	0.3659	0.0004
10	2		0.5397	0.3669	600	400	90	0.8511	0.3667	0.0002
10	2		0.5397	0.3669	600	400	90	0.8488	0.3657	0.0012
10	2		0.5369	0.3650	600	400	90	0.8465	0.3647	0.0003
	$Fe_2(SO_4)_3 + HNO_3$									
	grm.	cm^3								
10	2	5	0.5384	0.3662	800	500	105	0.8494	0.3661	0.0001
10	2	5	0.5384	0.3662	800	500	105	0.8483	0.3655	0.0007
10	2	5	0.5371	0.3652	600	400	90	0.8455	0.3643	0.0009
10	2	5	0.5363	0.3645	600	400	90	0.8439	0.3636	0.0009

* See figure p. 12.

It is obvious that so far as the treatment in blank is concerned the degree of dilution had been reached at which no significant volatilization of the bromine takes place. We proceeded, therefore, to make the actual separation, the only change in conditions being the addition of 0.5 grm. of potassium iodide, which was especially prepared and used in solution as described in the paper to which reference has been made. The boiling was continued until red litmus paper, moistened and held in the escaping steam for a minute or two, showed no reaction for iodine.

TABLE X.

H_2SO_4 [1 : 1].	KI.	$NaNO_2$ used in generator.		KBr = HBr taken.		Initial volume.	Final volume.	Time in min.	AgBr = HBr found.		Error in HBr.
cm^3	grm.	grm.		grm.	grm.	cm^3	cm^3		grm.	grm.	grm.
10	0.5	2		0.5371	0.3652	600	500	20	0.8358	0.3601	0.0051—
10	0.5	2		0.5367	0.3647	600	500	30	0.8337	0.3592	0.0055—
10	0.5	2		9.5365	0.3647	600	500	20	0.8309	0.3580	0.0067—
		$Fe_2(SO_4)_3 + HNO_3$									
		grm.	cm^3.								
10	0.5	2	5	0.5373	0.3653	700	550	75	0.8170	0.3520	0.0133—
10	0.5	2	5	0.5375	0.3655	700	550	60	0.8171	0.3520	0.0135—

In the comparison of the results of these experiments with those of Table IX, it is plain that, though the time of exposure to the boiling temperature is much shorter, the evolution of the iodine is attended by a not inconsiderable disappearance of bromine. This loss is greater in those tests in which the oxidation is produced by the combined action of nitric acid and the ferric salt. It is plain that in this form the method is useless. We tried next the effect of reducing the quantities of the reagents used by one-half, keeping the volume of the liquid the same, and, finding that the process, conducted otherwise exactly as described above, yielded under these new conditions 0.1825 grm. of hydrobromic acid instead of 0.1827 grm. taken, we began a series of experiments designed to test the effect of varying the amounts of sulphuric acid

present. The other conditions were kept unchanged. Table XI contains the record of experiments of this sort in which the oxidizing effect was secured by the action of nitric acid and a ferric salt. In Table XII are given the results of experiments in which the fumes generated by the action of sulphuric acid upon sodium nitrite were passed into the liquid to set the iodine free.

TABLE XI.

H_2SO_4 [1 : 1].	KI.	$Fe_2(SO_4)_3 + HNO_3$		KBr = HBr taken.		Initial volume.	Final volume.	Time in min. approximately.	AgBr = HBr found.		Error in HBr.
cm^3	grm.	grm.	grm.	grm.	grm.	cm^3	cm^3		grm.	grm.	grm.
5	0.5	2	3	0.5514	0.3748	650	500	90	0.8285	0.3570	0.0178—
4	0.5	2	3	0.5510	0.3745	650	500	90	0.8378	0.3610	0.0135—
3	0.5	2	3	0.5514	0.3748	650	500	90	0.8463	0.3647	0.0101—
2	0.5	2	3	0.5504	0.3741	650	500	90	0.8521	0.3672	0.0069—
1	0.5	2	3	0.5508	0.3744	650	500	90	0.8554	0.3686	0.0058—

It is plain that in both processes the loss of bromine diminishes as the amount of sulphuric acid decreases. In the presence of nitric acid and ferric sulphate the point is never reached, within the limits of our experimentation, at which the error is brought within allowable bounds. This mode of attempting the separation of bromine and iodine we therefore abandoned.

On the other hand the nitrous acid process, fairly successful when the sulphuric acid present is restricted to 5 cm^3 of the half and half acid (or to 2.5 cm^3 of the strong acid), is established as trustworthy when the sulphuric acid present is held within the limits of 2 cm^3 to 4 cm^3 of the [1 : 1] mixture. The mean error of thirteen determinations in which the proportions last mentioned were preserved is 0, lying between extremes of 0.0008 grm. — and 0.0007 grm. +. When the quantity of sulphuric acid is still further diminished there appears to be a slight tendency to show an apparent excess of the bromide, due in all probability to the retention of a little

TABLE XII.

H_2SO_4 [1 : 1].	KI.	$NaNO_2$ used in generator.	KBr = HBr taken		Initial volume.	Final volume.	Time in minutes.	AgBr = HBr found.		Error in HBr.
cm³	grm.	grm.	grm.	grm.	cm³	cm³, never less than 500.	Ab't 30	grm.	grm.	grm.
5	0.5	2	0.5374	0.3654	600	. . .	. .	0.8460	0.3645	0.0009−
5	0.5	2	0.5375	0.3655	600	. . .	. .	0.8447	0.3639	0.0016−
5	0.5	2	0.5365	0.3647	600	. . .	. .	0.8473	0.3651	0.0004+
5	0.5	2	0.5361	0.3644	650	. . .	. .	0.8461	0.3645	0.0001+
5	0.5	2	0.5106	0.3471	650	. . .	. .	0.8070	0.3478	0.0007+
5	0.5	2	0.5506	0.3743	650	. . .	. .	0.8645	0.3725	0.0018−
4	0.5	2	0.5371	0.3652	650	. . .	. .	0.8466	0.3647	0.0005−
4	0.5	2	0.5377	0.3655	650	. . .	. .	0.8473	0.3651	0.0004−
4	0.5	2	0.5508	0.3744	650	. . .	. .	0.8676	0.3737	0.0007−
3	0.5	2	0.5371	0.3652	650	. . .	. .	0.8459	0.3644	0.0008−
3	0.5	2	0.5365	0.3647	650	. . .	. .	0.8465	0.3647	0.0000
3	0.5	2	0.5368	0.3649	650	. . .	. .	0.8486	0.3656	0.0007+
3	0.5	2	0.5364	0.3646	650	. . .	. .	0.8471	0.3650	0.0004+
3	0.5	2	0.5505	0.3742	650	. . .	. .	0.8690	0.3744	0.0002+
3	0.5	2	0.0576	0.0391	650	. . .	. .	0.0915	0.0394	0.0003+
3	0.5	2	0.0552	0.0375	650	. . .	. .	0.0883	0.0380	0.0005+
2	0.5	2	0.5366	0.3647	650	. . .	. .	0.8478	0.3654	0.0007+
2	0.5	2	0.5369	0.3650	650	. . .	. .	0.8472	0.3651	0.0001+
2	0.5	2	0.5515	0.3747	650	. . .	. .	0.8687	0.3742	0.0005−
1	0.5	2	0.5367	0.3648	650	. . .	. .	0.8494	0.3660	0.0012+
1	0.5	2	0.5366	0.3647	650	. . .	. .	0.8490	0.3658	0.0011+
1	0.5	2	0.5368	0.3649	650	. . .	. .	0.8492	0.3659	0.0010+
1	0.5	2	0.5515	0.3749	650	. . .	. .	0.8763	0.3776	0.0027+

combined iodine in the solution. The best proportion for practical use is probably 3 cm³ of the half and half acid to an initial volume not less than 600 cm³ — the amount lying midway between the proportions with which divergences begin to be noted.

Other test determinations were made along the same lines, excepting that, instead of generating the nitrous fumes outside the liquid under treatment, pure sodium nitrite was introduced directly into the solution. The nitrite was prepared free from halogens by adding to its solution a little silver nitrate, acidulating distinctly with nitric acid, and filtering off the little silver chloride thus precipitated, together with a small amount of silver nitrite thrown down at the same time. The strength of the solution thus prepared was determined by acting upon a definite portion with ferrous sulphate

in excess and titrating the residual ferrous salt with potassium permanganate. The details of these experiments are given in Table XIII.

TABLE XIII.

H_2SO_4 [1:1].	KI	$NaNO_2$ in the liquid.	KBr = HBr taken.		Initial volume.	Final volume.	Time in minutes.	AgBr = HBr found.		Error in HBr.
cm³	grm.	grm.	grm.	grm.	cm³	cm³, never below 500 cm³.	Ab't 30	grm.	grm.	grm.
3	0.5	0.35	0.5508	0.3745	650	. . .	. .	0.8689	0.3744	0.0001−
3	0.5	0.35	0.5513	0.3747	650	. . .	. .	0.8694	0.3746	0.0001−
3	0.5	0.35	0.5513	0.3747	650	. . .	. .	0.8699	0.3748	0.0001+
3	0.5	0.35	0.3005	0.2042	650	. . .	. .	0.4746	0.2045	0.0003+
3	0.5	0.35	0.2759	0.1875	650	. . .	. .	0.4358	0.1878	0.0003+
3	0.5	1.75	0.5513	0.3747	650	. . .	. .	0.8705	0.3750	0.0003+
3	0.5	1.75	0.5510	0.3746	650	. . .	. .	0.8707	0.3751	0.0005+

The mean error of these seven determinations is 0.0002 grm. +, lying between the extremes 0.0005 grm. + and 0.0001 grm. −. In the first five of these determinations enough nitrite was employed to break up one and a half times the amount of iodide taken, if the action is supposed to go to the point of setting NO free. In the last two experiments, eight times the quantity of the nitrite theoretically thus called for was taken with no apparent change in the effect.

That iodine may be removed with reasonable accuracy from mixtures of iodides and bromides without disturbing the bromine is evidently established; and, inasmuch as the proportion in which the reagents are taken in the corresponding process for the separation of chlorine from iodine lie far within the limits found applicable to the bromine separation, it would be natural to suppose that in the presence of a chloride associated with the bromide the sum of the hydrobromic and hydrochloric acids would be given with exactness under the conditions suitable for the estimation of the former. We deemed it best, however, to submit this point to the test of experiment. The result substantiates the presumption.

TABLE XIV.

H_2SO_4 [1:1].	KI.	$NaNO_2$.	KBr.	KCl.	Theory for AgCl + AgBr.	AgCl + AgBr found.	Error in silver salt.	Error calculated as HBr.	Error calculated as HCl.
cm^3.	grm.	grm.	grm.	grm.	grm.	grm.	grm.	grm.	grm.
3	0.5	0.35	0.5517	0.4981	1.8280	1.8262	0.0018—	0.0008—	0.0006—
3	0.5	0.35	0.5511	0.4980	1.8268	1.8253	0.0015—	0.0005—	0.0004—

It is plain, in conclusion, that of the two methods which we have studied, though both are applicable to the separation of chlorine from iodine, but one is utilizable for the separation of bromine from iodine, and that under modified conditions. With the necessary modifications, however, it is good, and easily applied. It may be briefly summarized as follows: The neutral solution containing the bromide and iodide is diluted to 600 cm^3 or 700 cm^3 (instead of 400 cm^3, which was found to be a sufficient dilution in the case of the separation of chlorine from iodine), 1 cm^3 to 1.5 cm^3 of strong sulphuric acid, or, better, 2 cm^3 to 3 cm^3 of the mixture made by diluting the acid with an equal volume of water (instead of 10 cm^3 of the 1 : 1 mixture employed in the chlorine separation), are added, a sufficient amount of pure sodium or potassium nitrite is introduced (or, if it is preferred, the gas generated by the action of dilute sulphuric acid upon the ordinary nitrite and introduced from the outside may be employed instead,) and the liquid is boiled, after trapping the flask as described, until the color has vanished and the escaping steam no longer gives to red litmus paper the color characteristic of iodine. The residual liquid is treated with an excess of silver nitrate, and the precipitated bromide filtered off, dried, and weighed. The process of boiling need not extend beyond a half hour, or a little more, and care should be taken that the volume of the liquid shall never be less than 500 cm^3. We have not dealt with quantities of the potassium bromide and iodide larger than 0.5 grm. each, approximately. The presence of 0.5 grm. of potassium chloride does not affect the sharpness of the separation.

V

A RAPID METHOD FOR THE DETECTION OF IODINE, BROMINE, AND CHLORINE IN PRESENCE OF ONE ANOTHER.

By F. A. GOOCH and F. T. BROOKS.*

THE conditions under which iodine may be set free and separated quantitatively from hydrochloric and hydrobromic acid by the action of nitrous acid upon the acidulated solutions of the haloid salts have been recently studied in this laboratory.† We have endeavored in the work which is here described to so modify the quantitative process that the same principles of action may be applied rapidly and easily to the qualitative detection of iodine, bromine, and chlorine, without decreasing to too great a degree the delicacy of the indications. It was found in the work referred to that when sulphuric acid is added to the aqueous solution of a soluble chloride, bromide, and iodide, with care to keep the proportion of acid within certain limits and the dilution of the liquid sufficient, no very appreciable volatilization of bromine or chlorine takes place during the complete expulsion of the iodine by boiling. For the quantitative separation of the iodine of 0.5 grm. of potassium iodide from a solution containing 0.5 grm. of potassium bromide and 0.5 grm. of potassium chloride it was found best to use from 1 to 2 cm^3 of strong sulphuric acid, and to introduce into the solution, measuring approximately 700 cm^3 in volume, 0.5 grm. of potassium nitrite, or its equivalent in nitrous fumes. It is obvious that work upon this scale is undesirable in rapid qualitative testing. For such purpose it is not a matter of moment that a portion of the substances looked for escapes

* From Am. Jour. Sci., xl, 283.

† Am. Jour. Sci., xxxix, 293, and xl, 145. This volume, pp. 18, 37.

the reaction, provided enough is left to furnish the indication sought. We planned, therefore, to attempt the separation of iodine from bromine and chlorine by applying the reaction just mentioned to small amounts of liquid in test-tubes, in the hope that the known losses of chlorine and bromine under the conditions would be proportioned to the strength of the solution, or, in other words, that when the amounts of bromine and chlorine were very small they would escape volatilization, or that when large a sufficiency would remain to give strong tests.

The detection of the iodine is, of course, simple. We chose for this purpose the reaction with sulphuric acid and potassium nitrite. If the amount of iodine present is large it shows at once in this test, and the same portion may be treated further to separate the iodine. If the amount of iodine is small it may be found, as usual, by shaking the liquid with chloroform or carbon disulphide or other appropriate solvent for iodine; or, in this case also, the portion under test may be utilized, if it is desirable, for the separation of the iodine, and for the detection of this element recourse may be had to the exposure of red litmus paper to the fumes of the boiling solution according to methods prescribed in the work referred to above upon the quantitative separation of the iodine, — the paper taking on a gray-blue color when exposed to very minute traces of the vapor of iodine, and a proportionately deeper color as the amount of iodine increases. After the iodine is separated, bromine and chlorine are easily found if present. We selected as the most available method for detecting bromine the action of sodium hypochlorite upon the acid solution and shaking with the proper solvent. For the detection of chlorine we make use of a modification of the well known chlorochromic anhydride test.

As a preliminary step to the investigation of the reliability of our method of separating iodine from bromine, tests were made, for the purpose of securing definite points of comparison, upon the degree of delicacy of the hypochlorous acid test for bromine. In these tests measured amounts of a solution of potassium bromide were drawn from a burette into test-tubes. To each portion were added a few drops of sulphuric acid, the

liquid was diluted with distilled water to the level of a mark upon the tube indicating a volume of 10 cm^3, 0.5 cm^3 of chloroform, or of white carbon disulphide were introduced, and the whole was shaken after the addition of a drop of a dilute solution of sodium hypochlorite. The results of these tests are as follows: —

KBr taken.	Total volume.	Ratio of KBr to total volume.	Color test in chloroform.	Color test in carbon disulphide.
grm.	cm^3			
0.0010	10	1: 10000	Strong.	. . .
0.0005	10	1: 20000	Pronounced.	. . .
0.0004	10	1: 25000	Pronounced.	Strong.
0.0003	10	1: 33000	Faint.	Pronounced.
0.0002	10	1: 50000	Trace.	Faint.
0.0001	10	1:100000	Doubtful.	Trace.
0.0001	10	1:100000	None.	Trace.
0.00007	10	1:140000	. . .	Doubtful.
0.00007	10	1:140000	. . .	Doubtful.
0.0004	5	1: 12500	Strong.	. . .
0.0003	5	1: 16000	Strong.	. . .
0.0002	5	1: 25000	Pronounced.	. . .
0.0001	5	1: 50000	Trace.	. . .
0.00007	5	1: 70000	None.	Faint.
0.00003	5	1:140000	. . .	Doubtful.

From these results it is plain, as Fresenius has pointed out, that clear white carbon disulphide is the more sensitive reagent, the delicacy of the test extending distinctly to one part in fifty thousand when chloroform is the solvent for bromine and to one part in one hundred thousand when carbon disulphide is employed.

In the following series of tests the bromide was subjected to the same treatment which it must undergo were iodine actually present and expelled as we proposed. To the solution of the bromide in a test-tube were added a few drops of dilute sulphuric acid and a few drops of a solution of potassium nitrite. The liquid was boiled, cooled, and treated with sodium hypochlorite as in the former tests, excepting that even after boiling for some time it was found to be necessary to introduce more of the hypochlorite than before to overcome the nitrous acid remaining in solution and to set free the bromine.

KBr taken.	Total volume.	Ratio of KBr to total volume.	Color test in carbon disulphide.
grm.	cm³		
0.0010	10	1 : 10000	Strong.
0.0005	10	1 : 20000	Pronounced.
0.0004	10	1 : 25000	Pronounced.
0.0003	10	1 : 33000	Faint.
0.0002	10	1 : 50000	Faint.
0.0001	10	1 : 100000	Doubtful.
0.00007	10	1 : 140000	None.
0.00007	5	1 : 70000	Trace.

Evidently the presence of nitrous acid and the treatment by boiling do not interfere seriously with the delicacy of the test. The experiments of the following series were made similarly, excepting that potassium iodide was added in varying amount to the solution of the bromide. In these tests a spiral of platinum wire was introduced into the test-tube to prevent too violent ebullition, and at intervals during the boiling the nitrite was added in solution, drop by drop, until the iodine was entirely expelled, care being taken to add a little more sulphuric acid toward the end of the separation to ensure completeness of action. The colorlessness of the liquid in the test-tube after this treatment is a fair indication of the entire expulsion of iodine, but when large amounts of bromide are present free bromine will color the liquid. Salts of iron or other substances which possess color naturally interfere likewise. In such

KI taken.	KBr taken.	Total volume.	Ratio of KBr to total volume.	Color in carbon disulphide.
grm.	grm.	cm³		
0.1000	0.0010	10	1 : 10000	Pronounced.
0.1000	0.0004	10	1 : 25000	Pronounced.
0.1000	0.0003	10	1 : 33000	Pronounced.
0.1000	0.0002	10	1 : 50000	Faint.
0.1000	0.0002	10	1 : 50000	Faint.
0.1000	0.0001	10	1 : 100000	None.
0.0500	0.0005	10	1 : 20000	Pronounced.
0.0400	0.0004	10	1 : 25000	Pronounced.
0.0300	0.0003	10	1 : 33000	Pronounced.
0.0200	0.0002	10	1 : 50000	Faint.
0.0100	0.0001	10	1 : 100000	None.
0.1000	0.00007	5	1 : 70000	Trace.
0.0070	0.00007	5	1 : 70000	Trace.

cases, and indeed in all cases, the action of the escaping steam upon red litmus paper is decisive. In the experiments here recorded this test was applied to determine the absence of iodine from the liquid. The residue after the expulsion of the iodine was treated as usual with sodium hypochlorite and shaken with carbon disulphide.

These results indicate obviously that although the bromine is volatilized to some extent with the iodine it is nevertheless the case that the proportionate amount of bromine removed is dependent upon the absolute amount present, and that enough bromine always remains to permit correct inference as to the quantity originally present, the color test being more or less marked according as much or little bromide was in the solution at the start. The delicacy of the test is a trifle less than that in which the bromide is alone present and not subjected to the treatment which we employ to remove iodine, but the detection of one part of potassium bromide in fifty thousand is certain, and that of one part in seventy thousand possible. It appears, furthermore, that the increase in the amount of iodine present is without effect upon the sensitiveness of the test; for the bromine in 0.00007 grm. of potassium bromide was as easily found in the residue remaining after the expulsion of the iodine from 0.1 grm. of potassium iodide as in that left after the expulsion of the iodine from 0.0070 grm. of the same salt, and the indications in the experiments in which the ratio of the iodine to the bromine remained the same while the absolute amounts of both varied are precisely the same as those of the experiments in which the maximum amount of iodine remained unchanged throughout the variations in the amount of bromide used. The maximum amount of potassium iodide employed in these tests was 0.1 grm., but there is no reason to suppose that this amount is not far below the maximum which may be successfully handled in this process.

For the detection of chlorine we modified the well-known chlorochromic anhydride process so that the distillation may be performed in an ordinary test-tube. The substance to be tested is, if solid, placed in a large test-tube—15 cm.×2 cm. is a good

size — and treated with sulphuric acid and potassium dichromate in the manner to be described. The substance, if a liquid, is rendered alkaline, if necessary, by sodium carbonate and evaporated to dryness in the test-tube with care to remove all moisture from the sides of the tube. This operation is effected without trouble if the tube is inclined, as much as is possible without spilling the liquid, and agitated continually while the flame is applied to the higher parts. The evaporation effected, a little powdered potassium dichromate is introduced through a funnel with care to prevent its touching the upper parts of the tube, two or three cubic centimeters of strong sulphuric acid are added, and a trap consisting of a straight two-bulbed drying-tube cut off about an inch from the large bulb is hung in the mouth of the test-tube, the precaution having been first taken to moisten the interior of the bulbs with water without wetting the wide, straight portion which hangs within the test-tube. If a chloride is present the evolution of chlorochromic anhydride begins as soon as this sulphuric acid touches the dry salts in the bottom of the tube, and gentle heating, with a little agitation, quickly completes the evolution of the chlorine compound. It is the function of the moisture in the bulbs to decompose the fumes of the chlorochromic anhydride and to retain the chromic acid thus produced. When more than a mere trace of chlorine is present the yellow drops produced in the moistened bulbs are, in the absence of a bromide, sufficiently indicative of the presence of chlorine in the original substance, but the delicacy of this test is much increased by washing out the bulbs with a little distilled water and adding to the solution, as Wiley recommends,* a few drops of a solution of lead acetate, which precipitates the yellow chromate or intensifies the color of the solution according to the amount of chromic acid acting. It often happens, when the temperature of the liquid in the test-tube rises a little higher than need be, that fumes of sulphuric acid pass into the bulbs to such an extent as to produce a white precipitate of lead sulphate when the lead acetate is subsequently added. In such cases the lead

* Am. Chem. Jour., ii, 248.

sulphate is easily dissolved by the addition of a little ammonic acetate in saturated solution, and gentle heating, and on cooling the yellow chromate is either precipitated or simply colors the liquid. It is advisable, however, as our experience proved, not to employ more of the ammonic acetate than the occasion requires, as it undoubtedly exerts some solvent action upon the lead chromate as well as upon the sulphate.

We proceeded to test in the manner described the applicability of this process by first testing the action upon solutions of pure potassium chloride.

KCl taken.	Final volume.	Reaction obtained.
	cm^3	
0.0080	5	Marked precipitation.
0.0020	5	Marked precipitation.
0.0010	5	Distinct precipitation.
0.0005	5	Distinct color.
0.0004	5	Faint color.
0.0003	5	Faint color.
0.0002	5	Faintest color.
0.0001	5	Doubtful.
0.0001	5	None.
0.0001	5	None.

It appears, therefore, that the chlorine in 0.0005 grm. of potassium chloride is found certainly, and that indications of chlorine in amounts of the chloride ranging as low as 0.0002 grm. are fairly evident in tests made upon the pure substance taken in solution, evaporated, and treated as described.

The effect of submitting the solution of the chloride containing also a known amount of potassium iodide to the process previously described for liberating the iodine, of then neutralizing the solution with sodium carbonate, evaporating to dryness, and treating with sulphuric acid and potassium dichromate, is shown in the following record. The potassium iodide used in these tests was prepared free from chlorine by the action of resublimed iodine upon iron wire and subsequent treatment with pure potassium carbonate. The nitrite was freed from chlorine by adding to its solution a little silver nitrate, faintly acidulating with nitric acid, and

filtering off the chloride precipitated with a small amount of the nitrite.

KI taken.	KCl taken.	Final volume.	Reaction obtained.
grm.	grm.	cm³	
0.1	0.0020	5	Distinct precipitation.
0.1	0.0010	5	Distinct color.
0.1	0.0005	5	Faint color.
0.1	0.0004	5	Faint color.
0.1	0.0003	5	Faintest color.
0.1	0.0002	5	Faintest color.
0.1	0.0001	5	None.

The distinctness of the color obtained in this process seems to be diminished a little by the process of liberating the iodine, but the lowest reach of the test is not very materially different from that made upon the pure chloride. In the following similar tests made with mixtures containing beside the chloride potassium bromide alone, or the bromide as well as iodide, the phenomena observed were the same, excepting that the fumes of the bromine evolved when much bromide is present rise with the chlorochromic anhydride and, dissolving in the film of moisture in the trap, give to it their own characteristic color, and so obscure the effect of chromic acid. In these experiments, therefore, the washings of the bulbs were first rendered faintly ammoniacal and gently heated to destroy the free bromine, and then the solution was acidified with acetic

KI taken.	KBr taken.	KCl taken.	Final volume.	Reaction obtained.
grm.	grm.	grm.	cm³	
. .	0.1	0.0030	5	Marked precipitation.
. .	0.1	0.0020	5	Distinct precipitation.
. .	0.1	0.0010	5	Distinct color.
. .	0.1	0.0005	5	Faint color.
. .	0.1	0.0005	5	Faint color.
. .	0.1	0.0004	5	Faintest color.
. .	0.1	0.0003	5	Doubtful color.
. .	0.1	0.0002	5	Doubtful color.
. .	0.1	0.0001	5	None.
0.1	0.1	0.0010	5	Distinct color.
0.1	0.1	0.0010	5	Distinct color.
0.1	0.1	0.0010	5	Distinct color.

boiled with constant agitation. When the color of iodine disappears from the fumes and the solution, a drop or two more of sulphuric acid, and of the nitrite, are again added, and the boiling is repeated. When the escaping steam no longer gives to red litmus paper the characteristic gray-blue color due to the action of iodine, the process of separation is complete.

A portion of the solution thus prepared is tested for bromine by cautiously adding a dilute solution of sodium hypochlorite and shaking with colorless carbon disulphide.

The test for chlorine is made in a second portion of the solution from which the iodine has been removed. The liquid is neutralized with sodium carbonate or hydrate free from chlorine, evaporated to dryness in a test-tube and treated as described with sulphuric acid and potassium dichromate, the fumes of the chlorochromic anhydride which arise on gentle warming being condensed and converted to chromic acid by the film of moisture upon the interior walls of the trap. The trap is washed out with a very little distilled water (5 cm^3 are enough), and the washings made slightly ammoniacal to destroy free bromine, if necessary, and after gentle warming again acidified, are tested with lead acetate. If the yellow chromate is precipitated the presence of chlorine in the original substance is proved. If the precipitate is white, as is very likely to be the case, a few drops of a saturated solution of ammonium acetate are added with caution, and the whole is gently warmed to dissolve the white sulphate. On cooling the solution and shaking (or immediately if much chromic acid has been formed), the yellow chromate falls, or gives color to the solution according as the chloride was originally present in large or small amount.

The process is rapid and sufficiently exact for qualitative testing in general.

VI

ANALYSIS OF RHODOCHROSITE FROM FRANKLIN FURNACE, NEW JERSEY.

By P. E. BROWNING.*

THE specimen of rhodochrosite, an analysis of which is here given, was collected for the Yale Museum some two or three years since and was furnished to writer for examination by Professor E. S. Dana. It has a massive, cleavable structure and a bright pink color. Franklinite and willemite are immediately associated with it. The method of analysis was as follows:

A portion of the mineral was dissolved in hydrochloric acid, evaporated to dryness to separate any silica present. The filtrate from silica was treated either with sodic acetate or ammonium hydrate, and the iron separated and weighed. After the separation of the iron, the zinc was precipitated as sulphide by hydrogen sulphide in acetic acid solution. The filtrate from sulphide of zinc was treated with bromine water, by which method the manganese comes down as black oxide. In two determinations ammonia was used with the bromine water to bring about the same result. In all these cases the black oxide was dissolved and reprecipitated to avoid any holding back of lime. The black oxide in every case was dissolved by sulphurous and hydrochloric acids, precipitated as phosphate and weighed after ignition as pyrophosphate according to the method of Gibbs. The amount of manganese being large, two direct determinations were also made by Ford's method, which consists in boiling the mineral, after separating the silica, with strong nitric acid and potassium chlorate until green fumes cease to be given off. The black oxide is thus

* From Am. Jour. Sci., xl, 375.

directly precipitated and may be treated as above by Gibbs's method. These results were satisfactory in their agreement. The filtrate from black oxide of manganese was evaporated to about 300 or 400 cm^3, made ammoniacal, and calcium precipitated as oxalate, dissolved, and reprecipitated in same manner. The filtrate from both oxalate precipitations was evaporated (and in two cases the residue was ignited to free it from great excess of salts of ammonia) and precipitated as phosphate, dissolved in hydrochloric acid and reprecipitated in same manner with ammonia and a little hydrodisodic phosphate, ignited, and weighed as pyrophosphate. Each element was determined at least three times. Five determinations of manganese were made. Two analyses of the mineral were carried through in platinum dishes to avoid any contamination by silica in glass or porcelain. The amount of iron in ferrous condition was determined by dissolving a portion of mineral in sulphuric acid and titrating with a standard solution of potassium permanganate. Three determinations of carbon dioxide were made, taking 0.5 grm. portions, and a fourth in which 2 grm. were used agreed closely with the others. In these determinations the carbon dioxide was set free in suitable apparatus by the action of hydrochloric acid and heating, and weighed after absorption in potassium hydrate. The analysis is as follows:

Specific gravity = 3.47.

MnO	45.02 per cent.
CaO	11.28
ZnO	2.32
MgO	1.76
FeO	0.22
Fe_2O_3	0.16
SiO_2	0.32
CO_2	38.94
	100.02

The presence of silica suggested the possible presence of zinc silicate (Zn_2SiO_4) as impurity; accordingly there was

deducted from the ZnO found enough to balance the silica, and the remaining constituents were calculated to one hundred per cent. The result is given in I below.

I.		II.	
MnO . .	45.55 per cent.	$MnCO_3$ . .	73.78 per cent.
CaO . .	11.41	$CaCO_3$ . .	20.37
ZnO . .	1.48	$ZnCO_3$ . .	2.28
MgO . .	1.78	$MgCO_3$ . .	3.74
FeO . .	0.22	$FeCO_3$ . .	0.35
Fe_2O_3 . .	0.16	Fe_2O_3 . .	0.16
CO_2 . .	39.40		100.68
	100.00		

The hypothetical composition of the mineral, calculating the bases as carbonates, is given under II above. It will be seen that the amount of acid (CO_2) required to supply the bases exceeds the amount found by 0.68 per cent. The ratio of Mn : Ca : Mg = 6.4 : .44.

VII

ON THE SO-CALLED PEROFSKITE FROM MAGNET COVE, ARKANSAS.

By F. W. MAR.*

In 1877 it was snown by Knop,† that the supposed perofskite of the Kaiserstuhl, contained besides titanium a considerable amount (23 per cent) of niobium and tantalum, and he accordingly made it an independent species and named it very appropriately *Dysanalyte*. The analysis of the similar mineral from Magnet Cove, Arkansas, the results of which are given below, shows that it is also distinct from perofskite and is to be classed with dysanalyte. For the material for analysis I am indebted to the kindness of Professor E. S. Dana.

The method of analysis was as follows: 0.500 grm. of the carefully selected mineral were placed with about 15 cm^3 of concentrated sulphuric acid in a platinum crucible of 150 cm^3 capacity and, the whole being covered with a watch-glass that the progress of the decomposition might be easily observed, boiled for ten or fifteen minutes. The cooled product was poured into 600 or 700 cm^3 of cold water and allowed to stand over night or until the calcium sulphate was completely dissolved. A small residue was usually found and this was put through the same process. Any final residue is silica and sometimes a little tantalum or niobium oxide. The former was determined by evaporation with sulphuric and hydrofluoric acids and the remaining oxide was added to the main oxides.

The solution of the mineral was then made slightly alkaline with ammonia and the precipitated earth filtered off. The lime was thrown out of the concentrated filtrate as oxalate

* From Am. Jour. Sci., xl, 403.

† Zeitschr. Kryst., i, 284.

in hydrochloric acid, and before the precipitation of the magnesia by microcosmic salt. The combined earths were precipitated in a slightly acid solution by oxalic acid in order to separate from any uranium, the cerium and yttrium groups separated by the sodium sulphate process and each precipitated again as oxalate and weighed as oxide. As appears, the main portion of the rarer earths belongs to the yttrium group.

An attempt was made to take the atomic weight, but the result obtained, 190, is probably too high, the color showing that part of the sulphate was changed to a basic salt. This, however, with the color of the oxides, a reddish-brown, and the fact that the solutions do not yield an absorption spectrum, suggests that a chief portion of the earth is terbium oxide.

The result of the analysis is as follows:

Specific gravity = 4.18.

			Molec. ratio.		Quantiv. ratio.	
CaO	33.12	÷	56 = .593	.611 or 23 × 2	1.22	= 4
MgO	0.74	÷	50 = .018			
FeO	0.23	Fe_2O_3				1.52 or 3
Fe_2O_3	0.50	Fe_2O_3				
	5.66	÷	160 = .035			
$[Yt, Er, Tr]_2O_3$	5.42	÷	428 = .012	.050 or 2 × 6	.300	= 1
$[Ce, La, Di]_2O_3$	0.10	÷	328 = .003			
Nb_2O_5	4.88	÷	268 = .016	.027 or 1 × 10	.270	= 1
Ta_2O_5	5.08	÷	444 = .011			2.48 or 5
TiO_2	44.12	÷	82 = .538	.539 or 20 × 4	2.156	= 7
SiO_2	0.08	÷	60 = .001			
	99.53					

II

ON CERTAIN POINTS IN THE PRECIPITATION OF BARIUM AS THE SULPHATE.*

[illegible]

In the course of preliminary work on barium sulphate two conditions are usually observed—absence of excess of acid, and boiling of the precipitate before filtration. If these rules are not observed the precipitate is apt to pass through the filter. Usually, if the process be performed in a clear liquid, the solution will settle very slowly. By observing the precautions named, however, under circumstances favorable for a rapid precipitation, a liquid is soon obtained which settles rapidly and can be filtered in a few minutes. These general results were noticed in the first instance in the action of sulphuric acid upon solutions containing a very large amount of potassium chloride with hydrochloric acid in excess. In the course of five or ten minutes the precipitate had completely settled and was found to be of a distinctly crystalline character and much coarser than the usual form of precipitated barium sulphate.

At the time it was thought that the cause of this rapid subsidence was the alkaline salt present, and, accordingly, a series of experiments was made in which potassium, sodium and ammonium hydrochlorides were added in varying amounts to about 400 cm³ of water, hydrochloric acid added to more than acidity (but not in measured amounts), 0.5 gram of barium chloride introduced, and precipitation brought about by adding dilute sulphuric acid. Sometimes these precipitates settled rapidly, but as often came down in the familiar milky condition. Later, another series of experiments, in which the

* From Am. Jour. Sci., xli, 388.

different conditions were more carefully regulated, was made thus: in 400 cm^3 of water were dissolved 0.5 grm. of barium chloride, 10 cm^3 of strong hydrochloric acid, and amounts of the alkaline chlorides varying from 5 grms. to 0.05 grm., the whole being precipitated with 10 cm^3 of a solution of sulphuric acid made by diluting the concentrated acid with three parts of water. These precipitates all settled rapidly, and the variation in the amounts of alkali seemed to exert no very marked influence. Finally, these experiments seeming to point to hydrochloric acid as the influential factor, a series of experiments was made to test the effect of varying the amount of this acid. From a solution containing in 400 cm^3 0.5 grm. of barium chloride and amounts of hydrochloric acid varying from 1 cm^3 to 50 cm^3, the barium was thrown out by means of 10 cm^3 of dilute sulphuric acid. This series showed that the hydrochloric acid had a very marked effect upon the precipitation of the barium sulphate. When only one or two cubic centimeters of hydrochloric acid were present, the precipitate appeared immediately, in a milky condition, and settled slowly; as the amount of acid was increased, a point was soon reached where the precipitate was not so quickly apparent, but settled out much more quickly and in a coarser condition. With 10 cm^3 to 15 cm^3 of strong hydrochloric acid in the solution, the precipitate settled clear in ten or twelve minutes and was in excellent condition for filtration. When the solution contained 50 cm^3 of the acid, the precipitate settled clear in five minutes. Upon adding the sulphuric acid to such very acid solutions, no precipitate shows for a moment, but then it separates in beautiful crystalline condition and falls almost immediately. It can be safely filtered with or without pressure in ten minutes. In one instance, in the course of the experiments just detailed, 2 grms. of barium chloride were precipitated in the presence of 30 cm^3 of hydrochloric acid, the precipitate was allowed to settle clear, and was then filtered and washed, the whole operation being completed in seven minutes. This rapid subsidence of the precipitate is seen in hot solutions only — 75° C. being the

cipitation was brought about by adding 10 cm³ of the dilute sulphuric acid. The precipitates were filtered, after standing about ten minutes, upon asbestos felts in perforated platinum crucibles.

The results of these determinations indicate plainly a loss of barium sulphate, but inasmuch as the felts used had been made very thin and it had been subsequently observed that a small quantity of the sulphate could be collected in one of the filtrates of the series by giving a circular motion to the water, it was thought that the thinness of the felts might offer an explanation of the loss and of the varying results of the series. The following series was, therefore, made in exactly the same manner except that care was taken to have the felts carefully made and reasonably thick.

	$BaCl_2 \cdot 2H_2O$ taken.	$BaSO_4$ found.	Error.
	grm.	grm.	grm.
(7)	0.5014	0.4785	0.0004—
(8)	0.2227	0.2122	0.0005—
(9)	0.5003	0.4773	0.0004—
(10)	0.5046	0.4814	0.0004—

These results are uniform and indicate a trifling loss only; though in the filtrates of these experiments, also, a very slight, but, as it proved upon refiltering, unweighable amount of the sulphate could be collected. The precipitate in the last of these experiments was filtered off almost immediately after precipitation, and before it had completely subsided. In another case the whole operation, including the three weighings necessary was conducted to a finish in forty-five minutes.

In spite of the appearance of the trifling deposit in the filtrate, the deficiency in barium sulphate in these determinations was not greater than should be expected from the accepted solubility of that salt in water. To ascertain the effect of strongly acid solutions upon the solubility of barium sulphate the following determinations were made.

In experiment (11) the same amounts of the sulphuric and hydrochloric acids, 10 cm³ and 15 cm³ respectively, were used

	$BaCl_2 2H_2O$ taken.	$BaSO_4$ found.	Time in minutes between precipitation and filtration.	Error.
	grm.	grm.		grm.
(14)	0.0030	0.0024	120	0.0004–
(15)	0.0050	0.0046	150	0.0002–
(16)	0.0050	0.0023	5	0.0025–
		0.0043	60	0.0005–
(17)	0.0050	0.0031	5	0.0016–
(18)	0.0050	0.0040	10	0.0007–
(19)	0.0100	0.0078	10	0.0017–
(20)	0.0100	0.0085	15	0.0010–
(21)	0.0100	0.0083	30	0.0012–
(22)	0.0100	0.0087	60	0.0007–

From these results it would appear that the precipitation, in the presence of hydrochloric acid to the amount indicated, does not take place so rapidly when the amount of the barium salt is small, but that two or three hours are sufficient for reasonably complete separation of the precipitate in any case.

In all the experiments described above there was no attempt at a gradual admixture of the reagents but they were measured out and at once added to the solutions, the whole being well stirred. From the results obtained, it appears to be established, as regards the usual precautions in precipitating barium by means of sulphuric acid, that, contrary to former usage, it is highly advantageous to have the solution strongly acid with hydrochloric acid; that it is not necessary to add the reagents drop by drop, but that the whole quantity required to complete the reaction may be added at once; that ordinary quantities of barium salts, in presence of a considerable excess of sulphuric and hydrochloric acids, are precipitated completely and at once, but that when only a few milligrams are present, the precipitate requires more time to separate under the same conditions. Two or three hours are, however, sufficient, and in no case is the excessive time of twelve hours required.

In the light of the fact demonstrated in the preceding account, that hydrochloric acid may be introduced freely, and without detriment to the quantitative exactness of the precipitation of barium in the form of sulphate from pure solutions, it seemed desirable to look somewhat into the question as to

what the influence of a large excess of hydrochloric acid might be upon the well known contaminating effect of alkaline salts present during precipitation, especially as it is customary to attempt the purification of barium sulphate thrown down in the reverse of this process — the determination of sulphuric acid by means of a soluble barium salt — by digestion of the washed precipitate in hydrochloric acid. The following series of experiments was undertaken with this end in view. The details are shown in the tabular statement, precipitation being effected in the presence of free acid and the alkaline salt.

	$BaCl_2 \cdot 2H_2O$ taken.	$BaSO_4$ found.	Error.	HCl in solution.	Alkaline salts present.
	grm.	grm.	grm.	cm^3	grm.
(23)	0.5092	0.5032	0.0169+	110	$KClO_3$ 3
(24)	0.5027	0.4907	0.0107+	10	" 3
(25)	0.5026	0.4944	0.0154+	100	KCl 5
(26)	0.5045	0.4939	0.0122+	10	" 5
(27)	0.5020	0.4931	0.0137+	10	" 5
(28)	0.5013	0.4849	0.0061+	10	NaCl 5

From the results it is plain that, whatever may be the effect of digesting the washed precipitate in hydrochloric acid, the presence of this acid in large excess during precipitation in the presence of alkaline salts, does not prevent contamination of the precipitate. On the contrary, the greatest contamination seems to have occurred in those cases in which the acid was present to the largest degree, but, in view of the slight variation in contamination as compared with the great differences in the amount of acid employed, it does not appear probable that the increase of acid has very much to do with the amount of contamination.

It likewise seemed to be a matter of some interest in this connection, to investigate the process by which it is currently supposed* that barium sulphate carrying alkaline salts may be effectually purified, viz.: by the solution of the washed precipitate in strong sulphuric acid and reprecipitation by water. Accordingly the determinations of the following series were

* Fres., Quant. Anal., i, 547.

undertaken. The barium sulphate, precipitated from solutions containing 5 grm. of potassium chloride and 10 cm^3 of hydrochloric acid, was collected upon a filter, either paper or asbestos, and, after burning the paper or removing the precipitate from the asbestos (by tapping the crucible which held it and brushing out with a camel's-hair brush), was dissolved by warming with concentrated sulphuric acid in a large porcelain crucible and, after cooling, poured into water containing 15 cm^3 to 20 cm^3 of hydrochloric acid. The water into which the solutions in strong acid were poured was warmed with a view to diminish the milkiness of the precipitate, but care must be taken to keep the temperature below 60° C. to avoid danger of spattering on the addition of the sulphuric acid. In the last two of the experiments recorded a large amount of ammonium chloride was added to the water into which the solutions in acid were poured, but this appears to have been without influence upon the purification or the character of the precipitation. The precipitates, after settling clear, were filtered upon asbestos, ignited and weighed, the original felts being employed in those cases in which asbestos was used in the first instance. Those marked with an asterisk were gathered in the first filtration upon paper, the paper being burned in the crucible in which solution of the precipitate was subsequently effected. The remainder were filtered originally upon asbestos.

	$BaCl_2.2H_2O$ taken.	$BaSO_4$ found.	Error.
	grm.	grm.	grm.
(29)	0.5026	0.4746	0.0044−
(30)	0.5035*	0.4830	0.0022+
(31)	0.5016	0.4767	0.0024−
(32)	0.5025	0.4804	0.0050+
(33)	0.5046*	0.4829	0.0010+
(34)	0.5004	0.4825	0.0047+

These results show, evidently, that this process of purification is not satisfactory. It is possible that the losses observed may have been mechanical, and due to the violent action of the strong acid upon the water, but the excess in weight which

were made exactly like those of the last series, with the exception that the evaporation was effected by means of the Hempel apparatus.

	$BaCl_2 \cdot 2H_2O$ taken.	$BaSO_4$ found.	Error.
	grm.	grm.	grm.
(40)	0.5050	0.4824	0.0002+
(41)	0.5069	0.4838	0.0000
(42)	0.5041	0.4825	0.0021+
(43)	0.5021	0.4812	0.0018+
(44)	0.4033	0.4801	0.0005–

Though not an absolutely perfect process, the purification of barium sulphate by this method of solution and evaporation is evidently better, by far, than the old method of solution and reprecipitation by dilution.

IX

A METHOD FOR THE DETERMINATION OF ANTIMONY AND ITS CONDITION OF OXIDATION.

By F. A. GOOCH and H. W. GRUENER.*

BUNSEN'S method of determining qualitatively the condition of oxidation of salts of antimony, by boiling these substances in solution with potassium iodide and hydrochloric acid and noting whether the liquid takes the color of free iodine, has been applied successfully to the quantitative determination of antimony in its highest condition of oxidation by Weller,† who distils the iodine from the solution, collects it in the distillate and, determining it volumetrically, calculates from the amount of it found the antimonic salt which sets it free according to the equation

$$SbCl_5 + 2H\text{-}I = SbCl_3 + 2HCl + I\text{-}I.$$

The advantage of treating the residue, rather than the distillate, in analytical processes in general which involve distillation is so obvious as to constrain us to seek conditions under which Bunsen's reaction may be applied in such a manner that the antimony shall be held and estimated directly in the residue. The general plan of work was laid down in a similar process elaborated in this laboratory for the reduction of arsenic acid.‡ According to this process the arsenic to be reduced is taken in a solution of appropriate dilution, and treated with sulphuric acid in adjusted amount and an excess of potassium iodide. The liquid thus prepared is boiled to a definite degree of concentration, the iodine then remaining unexpelled, if any, is bleached by the very careful addition of dilute (centinormal)

* From Am. Jour. Sci., xlii, 213.

† Ann. Chem. (Liebig), ccxiii, 246.

‡ Gooch and Browning, Am. Jour. Sci., xl, 66. This volume, p. 30.

sulphurous acid, and the liquid is immediately diluted and neutralized. After cooling, the reduced arsenic is titrated by standard iodine in presence of starch.

We found in preliminary experimentation that the same general plan of treatment is available in the handling of antimonic compounds, but it is necessary to take precautions to prevent the deposition of the antimony from solution upon the addition of the sulphuric acid. Tartaric acid accomplishes this effect satisfactorily and does not, as the result proved, introduce undesirable complications. It transpired also that the dilution of the solution at which the crystalline iodide or oxy-iodide separates out during the boiling is greater than is the case when similar amounts of arsenic are dealt with. It appeared, for example, that concentration to 45 cm^3 was sufficient to cause crystallization and slight sublimation when the amount of antimonious oxide present (with excess of potassium iodide and 10 cm^3 of sulphuric acid, 1 : 1) was approximately 0.2 grm. Otherwise the process as employed in the reduction of arsenic appeared to be applicable to the similar treatment of antimony.

The following quantitative experiments were undertaken to discover the condition of concentration best suited to the reduction of antimonic salts under circumstances otherwise like those adapted to the reduction of arsenic, and to test the perfection of the process. Definite amounts of tartar emetic, purified by recrystallization, were used to make the antimonic salt to be afterward reduced, the antimony being raised to the highest degree of oxidation by titration with standard iodine after the addition of sodium tartrate (to prevent the precipitation of the antimony during the process of oxidation) and hydrogen sodium carbonate in the usual excess. In this process starch was sometimes employed to give the end reaction, and sometimes reliance was placed upon the appearance of the color of free iodine, experience having indicated that the use of the starch is not essential when the solutions are sufficiently small in volume, though as a matter of course, the correction demanded for the excess of iodine necessary to

nearly neutralized with sodium hydrate, made alkaline by hydrogen sodium carbonate added in an excess amounting to about 20 cm^3 of the saturated solution, was titrated with the standard (decinormal) iodine after the addition of a fresh portion of starch.

Table I contains the account of experiments in which the larger amounts of antimony were employed.

TABLE I.

Final volume.	Tartar emetic taken.	Sb_2O_3 taken.	Iodine used in final oxidation.	Sb_2O_3 found.	Error.
cm^3	grm.	grm.	grm.	grm.	grm.
100	0.5021	0.2178	0.3522	0.2004	0.0174—
80	0.5030	0.2181	0.3784	0.2153	0.0028—
60	0.5008	0.2172	0.3768	0.2144	0.0028—
60	0.5010	0.2173	0.3780	0.2151	0.0022—
60	0.5010	0.2173	0.3809	0.2168	0.0005—
55	0.5023	0.2178	0.3827	0.2178	0.0000
55	0.5015	0.2175	0.3806	0.2166	0.0009—
50	0.5007	0.2172	0.3814	0.2171	0.0001—
50	0.5039	0.2185	0.3839	0.2185	0.0000
45	0.5001	0.2169	0.3818	0.2173	0.0004+
45	0.5004	0.2170	0.3825	0.2176	0.0006+

The results of these experiments indicate unmistakably that complete reduction may be brought about under the conditions, but that concentration to a volume of from 45 cm^3 to 55 cm^3 during the boiling is not only advantageous but necessary. The mean error of the determination in which the final volume fell within these limits was zero between limits of 0.0009 grm. —, or 0.0006 grm. +. In both determinations in which a final volume of 45 cm^3 was reached, and in one of the experiments in which the final volume was 50 cm^3, the formation of the crystalline antimonious iodide or oxyiodide in the liquid was noted, and the deposition of a very slight sublimate of the same salt in the trap. It is evident, therefore, that it would be hazardous to attempt to push the concentration further. In all these experiments hydriodic acid was present in amount equivalent to 1.1 grm. of potassium iodide — 0.5 grm. introduced as iodine and 0.6 grm. introduced as such in the standard iodine where it plays the part of solvent.

In the experiments recorded in Table II, smaller amounts of antimony and correspondingly smaller quantities of the oxidizing solution were employed; otherwise, the same general mode of proceeding was followed. The limits of concentration fixed upon were, however, varied somewhat. The previous experiments showed plainly that anything like a complete reduction of the antimony could not be anticipated when the final volume was greater than 60 cm^3, and the experience with the smaller amounts of antimony treated in the second series pointed to the fact, as the work progressed, that for them the crystallization and sublimation did not occur until the concentration had brought about a decrease in volume to 35 cm^3. The limits of final volume were placed therefore, for these experiments, at 60 cm^3 and 35 cm^3. Centinormal iodine was used for the oxidations, and bleaching with sulphurous acid was found to be unnecessary, the amount of iodine liberated in these experiments being so small as to vanish in the concentration so completely that no color was visible (nor was it brought out by starch) after washing down the trap and cooling. There did remain a trace of color before the addition of the water, but this seemed to us to be due in all probability to the incipient formation of the antimonious iodide or oxyiodide which is decomposed by the action of more water. At all events, it disappeared on the addition of water and no reoxidation of the antimony was found subsequently.

TABLE II.

Final volume.	Tartar emetic taken.	Sb_2O_3 taken.	Iodine used in final oxidation.	Sb_2O_3 found.	Error.
cm^3	grm.	grm.	grm.	grm.	grm.
60	0.0500	0.0217	0.0239	0.0136	0.0081–
60	0.0500	0.0217	0.0258	0.0147	0.0070–
60	0.0500	0.0217	0.0261	0.0148	0.0069–
50	0.0500	0.0217	0.0316	0.0180	0.0037–
40	0.0500	0.0217	0.0385	0.0219	0.0002+
35	0.0500	0.0217	0.0380	0.0216	0.0001–
35	0.0500	0.0217	0.0381	0.0217	0.0000
35	0.0500	0.0217	0.0382	0.0218	0.0001+
35	0.0500	0.0217	0.0382	0.0218	0.0001+

These results show that for the smaller amounts of antimony the reduction was completed only by pushing the degree of concentration somewhat lower than was found to be necessary in treating the larger amounts. The only point in which these experiments differ essentially from those of the previous series is in the quantity of the iodine solution employed to effect this oxidation. So far as concerns the free iodine itself, the conditions are similar in both series; for the iodine is converted in both cases to hydriodic acid exactly equivalent in amount to the antimony acted upon. The potassium iodide which is added in the iodine solution produces by action upon the sulphuric acid present an excess of hydriodic acid, which is, of course, dependent upon the absolute amount of the iodine solution employed. The hydriodic acid is the active agent in the reduction of the antimony, and to the greater mass-action in the former series of experiments might be attributed the more complete reduction for equal degrees of concentration. Accordingly the determinations of Table III were made to put this point to the test. In these experiments the conditions were identical with those of the determinations of Table II, excepting that in every case 1 grm. of potassium iodide was added to the liquid before boiling, thus bringing the total amount of hydriodic acid present to an equality with that present in the experiments of Table I, in which the larger amounts of antimony were treated. The results of these experiments bear out completely the hypothesis concerning the mass-action of the hydriodic acid — the smaller amounts of antimony being completely reduced in the presence of the large excess of hydriodic acid even at a final volume of 60 cm^3 with a maximum error of 0.0002 grm.— .

TABLE III.

Final volume.	Tartar emetic taken.	Sb_2O_3 taken.	Iodine used in final oxidation.	Sb_2O_3 found.	Error.
cm^3	grm.	grm.	grm.	grm.	grm.
60	0.0500	0.0217	0.0378	0.0215	0.0002—
60	0.0500	0.0217	0.0379	0.0216	0.0001—
60	0.0500	0.0217	0.0379	0.0216	0.0001—

TABLE IV.

Final volume.	Tartar emetic taken.	Sb_2O_3 taken.	As_2O_3 taken.	Iodine used in first oxidation.	Iodine used in final oxidation.	Difference between the amounts of iodine used in the two oxidations.	Error in terms of	
							Sb_2O_3.	As_2O_3
cm^3	grm.	grm.	grm.	cm^3	cm^3	cm^3	grm.	grm.
50	0.1530	0.0870	0.0500	19.37	19.43	0.06+	0.0004+	0.0003—
50	0.1503	0.0855	0.0495	19.05	19.02	0.03—	0.0002—	0.0001—
50	0.1503	0.0855	0.0544	20.05	19.97	0.08—	0.0006—	0.0004—
50	0.1503	0.0855	0.0495	19.05	19.00	0.05—	0.0004—	0.0003+

It is plain that the error in these results, whether reckoned as falling upon the antimonious oxide or upon the arsenious oxide, is quite within the limits allowable in volumetric determinations by means of decinormal solutions. One point, however, in the determination of the combined amounts of antimony and arsenic by the method here proposed deserves special consideration. It has been shown in the work to which reference has been made that arsenic is reducible by the process outlined and determinable with accuracy by titration with iodine standardized against arsenious oxide. In this later work we show that antimony may be reduced similarly and estimated satisfactorily by titration against iodine standardized against tartar emetic. These two methods of standardizing do not yield identical results, and so we are confronted with an inherent error in the process for estimating antimony and arsenic at once, which cannot be overcome unless the individual amount of one or other constituent may be otherwise determined. If the determination of either the arsenic or antimony is possible it is, of course, easy to calculate with the use of the appropriate standard the amount of the solution of iodine which is really engaged in the oxidation of this particular constituent, and the remainder of the iodine actually employed, gauged by the second standard, will give the corrected amount of the second constituent.

In case no such correction is feasible it becomes a matter of interest to note the magnitude of possible error. Our experience, based upon many determinations throughout the course of the work detailed above, pointed to a difference in the

value of the two standards amounting to about one-half of 1 per cent. If, therefore, the weight of reduced oxide amounts to the maximum which we have experimented with — about 0.2 grm. — the greatest possible error will be 0.0010 grm. + or 0.0010 grm. —, according as the entire 0.2 grm. is antimonious oxide estimated by the arsenic standard, or arsenious oxide estimated by the tartar emetic standard. The essential features of the process which we propose for the reduction of antimony and the determination of its degree of oxidation are recapitulated briefly in the following statement.

The salt of antimony, not exceeding the equivalent of about 0.2 grm. of antimonious oxide, is titrated, in presence of 1 grm. of sodium tartrate and the usual excess of sodium hydrogen carbonate, by means of iodine standardized against tartar emetic. The result of this titration gives the amount of antimonious salt present. To the solution are then added 4 grm. of tartaric, dilute sulphuric acid, if necessary, to neutralization, an excess of 10 cm^3 of half and half sulphuric acid, and enough potassium iodide so that there shall be present of hydriodic acid the equivalent of a little more than 1 grm. of the iodide. The liquid is diluted to 100 cm^3, boiled in an Erlenmeyer beaker until the volume is decreased to 50 cm^3, the precaution being taken to introduce a platinum spiral to prevent bumping, and a trap, as described, to obviate mechanical loss. The color remaining after concentration, if there be any, is bleached by dilute sulphurous acid (approximately centinormal). The solution is nearly neutralized with sodium hydrate, treated with an excess of sodium hydrogen carbonate amounting to 20 cm^3 of the saturated solution, cooled, and titrated in presence of starch by the standard iodine. This final titration gives, of course, the entire amount of antimony present. The difference between the indications of the two titrations is the measure of the antimony in the higher condition of oxidation. The method as outlined is accurate and rapid, and so simple as regards manipulation that a number of determinations can be carried through simultaneously with the use of ordinary apparatus.

X

A METHOD FOR THE ESTIMATION OF CHLORATES.

By F. A. GOOCH and C. G. SMITH.*

It has been shown in recent work in this laboratory† that under conditions properly controlled, arsenic acid in excess is capable of expelling the iodine from hydriodic acid at the boiling temperature of the solution, being itself reduced correspondingly according to the equation

$$H_3AsO_4 + 2H\text{-}I = H_3AsO_3 + H_2O + I\text{-}I.$$

On cooling the liquid remaining after such treatment, and neutralizing, the arsenious oxide produced in the reaction may be reoxidized iodometrically in the usual manner, the iodine added to accomplish this purpose being the exact measure of the iodine originally present as hydriodic acid and expelled from the acid solution during the process of boiling.

If other sufficiently energetic and easily decomposable oxidizing agents are present at the same time with the arsenic acid, it would be natural to suppose that these substances will act similarly upon the hydriodic acid, and, furthermore, that the oxidizing power of the arsenic acid will not be called into play until that of the more unstable oxidizers has been exhausted. Chloric acid, for example, acts with great ease upon hydriodic acid, and it would be natural to suppose that in a mixture of chloric, hydriodic, and arsenic acids the mutual action of the chloric and hydriodic acids will be manifest first and will go on steadily to completion, and that when this effect is accomplished, and then only, the action of the arsenic acid, in liberating iodine from the residual hydriodic acid and in

* From Am. Jour. Sci. xlii, 220.

† Gooch and Browning: Am. Jour. Sci., xxxix, 188. This volume, p. 1.

lows: Portions of this solution were measured from a burette into Erlenmeyer beakers capable of holding 300 cm^3, 2 grm., approximately, of pure dihydrogen potassium arseniate were added in solution, 20 cm^3 of a mixture of sulphuric acid and water in equal volumes were introduced with enough water beside to increase the entire volume to a little more than 100 cm^3. A platinum spiral was introduced to secure quiet boiling, a trap made of a straight two-bulbed drying tube cut short was hung with the larger end in the neck of the flask,* and the liquid was boiled until the level had reached a mark upon the flask indicating a volume of 35 cm^3, experience having shown that this degree of concentration is sufficient and that it is best not to exceed it. The liquid remaining was cooled and nearly neutralized by sodium hydrate, acid potassium carbonate was added to alkalinity, 20 cm^3 of a saturated solution of this salt were added in excess, and the arsenious oxide in solution was titrated by standardized decinormal iodine in presence of starch. The iodine added in the reoxidation of the arsenious oxide was taken as the exact equivalent of the iodine expelled in boiling. Several closely agreeing determinations made in this manner served to fix the standard of the solution.

The action of chloric acid under similar conditions was tested by following out exactly the process employed in standardizing the iodide, with the exception that weighed amounts of potassium chlorate, purified by recrystallization, were also introduced and that the precaution was taken to have the potassium iodide present in every case to an amount at least eight and a half times as great as that of the potassium chlorate — this amount being a little more than the equivalent weight of the iodide referred to the chlorate. The experiments involved amounts of the chlorate ranging from 0.2 grm. to 0.01 grm., and quantities of the iodide varying from eight and a half to fifty times those of the chlorate. The results with all essential details are contained in the following table:

* See figure, p. 12.

H_2SO_4 [1 : 1] taken.	H_2KAsO_4 taken.	KI taken.	= I taken.	Iodine corresponding to As_2O_3 reduced.	Difference between iodine taken and iodine added to oxidize As_2O_3.	$KClO_3$ taken.	$KClO_3$ found, — that is, equivalent to I in column VI.	Error.
cm³	grm	grm.	grm.	grm.	grm.	grm.	grm.	grm.
20	2	2.0092	1.5356	2.2962	1.2394	0.2000	0.2000	0.0000
20	2	2.0092	1.5356	0.2978	1.2383	0.2000	0.1999	0.0001—
20	2	1.0380	0.7934	0.0570	0.7364	0.1185	0.1188	0.0003+
20	2	0.8706	0.6654	0.0435	0.6219	0.1000	0.1004	0.0004+
20	2	0.8706	0.6654	0.0429	0.6225	0.1000	0.1005	0.0005+
20	2	0.8706	0.6654	0.0435	0.6219	0.1000	0.1004	0.0004+
20	2	0.8706	0.6654	0.0435	0.6219	0.1000	0.1004	0.0004+
20	2	0.5023	0.3839	0.3208	0.0631	0.0100	0.0102	0.0002+
20	2	0.5023	0.3839	0.3201	0.0638	0.0100	0.0103	0.0003+
20	2	0.2009	0.1536	0.0889	0.0647	0.0100	0.0105	0.0005+
20	2	0.2009	0.1536	0.0903	0.0633	0.0100	0.0102	0.0002+
20	2	0.2009	0.1536	0.0903	0.0633	0.0100	0.0102	0.0002+
20	2	0.1339	0.1024	0.0405	0.0619	0.0100	0.0100	0.0000
20	2	0.1004	0.0768	0.0157	0.0611	0.0100	0.0099	0.0001—
20	2	0.1004	0.0768	0.0182	0.0586	0.0100	0.0095	0.0005—

The mean error of these determinations is a little less than 0.0002 grm +, between extremes of 0.0005 grm. + or 0.0005 grm. —, and the results are evidently excellent for an iodometric process in which titration is effected by decinormal solutions. An excess of iodide over an amount a little in excess of the equivalent proportion is without effect. The process is rapid and easy.

The paper upon the determination of iodine, to which reference has been made and upon which this process is based, prescribes corrections for the volatility of arsenious chloride and the slight deoxidation of arsenic acid when chlorides and bromides are also present in considerable amount. In this process, however, the amount of hydrochloric acid evolved from the maximum weight of chlorate treated — 0.2 grm. of the potassium salt — calls for a correction so small as to be insignificant.

XI

A METHOD FOR THE SEPARATION OF ANTIMONY FROM ARSENIC BY THE SIMULTANEOUS ACTION OF HYDROCHLORIC AND HYDRIODIC ACIDS.

By F. A. GOOCH and E. W. DANNER.*

A METHOD for the separation of arsenic from antimony based upon the difference in volatility of the lower chlorides was introduced originally by Fischer.† This method of treatment consisted in the reduction of the chlorides by means of ferrous chloride and the volatilization of the arsenic by repeated distillations of the mixture with hydrochloric acid of 20 per cent strength added in successive portions. The process has been subsequently modified by Hufschmidt ‡ by the substitution of gaseous hydrochloric acid, introduced in continuous current into the distilling mixture, for the aqueous acid, and later changed further and improved by Classen and Ludwig, § who employ ferrous sulphate, or ammonio-ferrous sulphate, in place of the less easily prepared ferrous chloride. In its latest form the method is exceedingly exact, but the conditions are such that the antimony in the residue must be determined gravimetrically. It has been our endeavor to so arrange the process that the determination of the antimony may be made by a rapid volumetric method, and this we have attempted to accomplish by substituting for the iron salt, which utterly precludes the direct volumetric estimation of the antimony, another reducer — hydriodic acid — which can interfere in no way with the subsequent determination of the antimony by the well known iodometric method.

* From Am. Jour. Sci., xlii, 308.

† Ann. Chem. (Liebig), 208, 182. ‡ Ber. Dtsch. chem. Ges., xvii, 2245.

§ Ber. Dtsch. chem. Ges. xviii, 1110.

dihydrogen potassium arseniate and a gram of potassium iodide were added in concentrated solution, the volume of liquid being made up to 100 cm^3 by the addition of strong hydrochloric acid. A brisk current of hydrochloric acid gas was passed into the solution through the tube sealed into the glass stopper of the flask until complete saturation was effected, and then the liquid was heated and distilled in the continuous current of hydrochloric acid gas until the volume of 30 cm^3 was reached. Iodine was evolved as soon as the

H_2KAsO_4 taken.	KI taken.	Volume		Color		Sb_2O_3 taken.	Sb_2O_3 found.	Error.
		Initial.	Final.	On cooling.	With starch.			
grm.	grm.	cm^3	cm^3			grm.	grm.	grm.
I.								
0.5	1.0	100	30	Pale yellow.	None.	0.2282	0.2271	0.0011—
0.5	1.0	100	30	None.	None.	0.2283	0.2266	0.0017—
II.								
0.5	0.5	120	50	None.	None.	0.2258	0.2235	0.0023—
0.5	0.5	100	50	Pale yellow.	None.	0.2252	0.2235	0.0017—
0.5	0.5	100	50	Pale yellow.	None.	0.2178	0.2163	0.0015—
0.5	0.5	100	50	Trace.	None.	0.2231	0.2231	0.0000
0.5	0.5	100	40	Trace.	None.	0.2261	0.2235	0.0026—
III.								
0.5	0.5	100	50	Pale yellow.	Faint.	0.2268	0.2265	0.0003—
0.5	0.5	100	50	Pale yellow.	Faint.	0.2306	0.2300	0.0006—
0.5	0.5	100	50	Pale yellow.	Faint.	0.2272	0.2264	0.0008—

liquid became warm and the greater part of it passed into the distillate with the first 10 cm^3. When the final concentration was reached the solution was in each case colorless, but on cooling there appeared in one of the two experiments of this set a pale yellow tint which vanished with the dilution involved in the transfer and washing from the flask previous to titration. The addition of starch to the cooled and diluted liquid developed no color. To the liquid were added 1 grm. of tartaric acid, to keep the antimony in solution during subsequent treatment, sodium hydrate nearly to neutrality, and

hydrogen sodium carbonate in excess amounting to about 20 cm^3 of the saturated solution; and the antimonious oxide in solution was titrated by decinormal iodine standardized against tartar emetic. The details of these experiments are given in Table I.

In Table II are comprised the accounts of experiments similar in general to those of Table I, excepting that the final volume after concentration was a little more, and the antimony was in every case oxidized in alkaline solution by standard iodine previous to the introduction of hydrochloric acid and distillation.

Table III includes the records of experiments similar in every respect to those of Table II excepting that as starch showed a slight color in the cooled liquid after distillation, the solution was treated with an excess of sulphurous acid which was subsequently oxidized exactly by standard iodine previous to neutralization and the final titration.

The same general phenomena were observed in all these experiments, and deficiencies in the amounts of antimony indicated, whether the element was present in the lower or higher degree of oxidation before distillation, appear in all, but most notably in the results of Tables I and II. These losses cannot be attributed, entirely at least, to mechanical transfer in the process, inasmuch as the greater losses are not associated with the greater concentrations; and, furthermore, according to our qualitative experiments made under the conditions of these determinations, no antimony, so far as we could observe, passes into the distillate. If the coloration of the liquid on cooling were due to the liberation of iodine by the action of air upon the hydriodic acid the iodine thus set free might be counted upon to oxidize a corresponding portion of the antimony in the neutralization, and so to occasion a deficiency in the indications of titration. Against this supposition, however, we have the evidence of experiment that the greatest losses are not found in those cases in which color was developed in the cooling liquid. Moreover, in all cases, excepting those of Table III, starch gave no test for free

iodine in the diluted liquid, though it must not be overlooked that the presence of a considerable amount of hydrochloric acid tends to impair the delicacy of the test. If, on the other hand, the color is not due altogether to free iodine it is difficult to account for its development unless it is caused by the formation of antimonious iodide as the solution of strong hydrochloric containing also hydriodic acid cools. On the whole, we are inclined to attribute at least a part of the apparent deficiency to the presence, at the time of neutralization, of a small amount of iodine chloride, which, in accordance with what is known of its modes of formation, might be formed by the oxidizing effect of the antimonic and arsenic oxides upon the mixed acids. At all events, it is evident that if iodine chloride were present we should expect to note the phenomena which we do see; it would give, in small quantity, little or no color to the liquid, would not show the starch reaction for free iodine in the acid solution, and would be destroyed with the formation of hydrochloric and hydriodic acids by the addition of sulphurous acid to the still acid liquid, leaving the antimony unchanged and determinable iodometrically in alkaline solution after the exact oxidation of the excess of sulphurous acid by iodine in acid solution; on the other hand it would act in alkaline solution like the free halogens and tend to diminish the antimony indicated by titration. Whatever the real cause or causes of the deficiency may be, it appears in the results of Table III that the treatment with sulphurous acid affects the indications favorably. The mean error of three closely agreeing determinations is 0.0006 grm. — and this is plainly within the limits of allowable variation in iodometric work with decinormal solutions.

It appears, therefore, that hydriodic acid may be made to serve satisfactorily as a substitute for the ferrous chloride of Fischer's original method, or for the ferrous sulphate of the modification of Classen and Ludwig, the determination of the residual antimony being perfectly practicable. The method of proceeding which we advocate is briefly summarized in the following statement: To the solution of the oxides of arsenic

and antimony, taken in amounts not exceeding 0.5 grm. of each, potassium iodide is to be added in a little more than the equivalent quantity, and enough strong hydrochloric acid to raise the entire volume of the solution to 100 cm^3. Hydrochloric acid gas is passed into the liquid to saturation as well as during the distillation to follow, and the distillation is carried on until the volume of the liquid decreases to 50 cm^3, or a little less. The liquid is cooled rapidly, treated first with an excess of sulphurous acid and then with iodine to the exact oxidation of the former reagent; and, after the addition of 1 grm. of tartaric acid to every 0.2 grm. of antimonious oxide, the acid present is nearly neutralized with sodium hydrate, the neutralization being completed by hydrogen sodium carbonate added in excess to an amount corresponding to 10 cm^3 of the saturated solution for every 0.1 grm. of antimonious oxide present. Titration with decinormal iodine standardized against tartar emetic gives the antimony quickly and with a fair degree of accuracy. The whole process requires about an hour and a half for completion.

XII

THE DETECTION AND DETERMINATION OF POTASSIUM SPECTROSCOPICALLY.

By F. A. GOOCH and T. S. HART.*

Bunsen and Kirchhoff originally determined the delicacy of the spectroscopic test for potassium by exploding in a darkened room a mixture of potassium chlorate with milk sugar, and observing the amount of finely divided chloride which it was necessary to diffuse through the given space in order to bring out unmistakably the spectrum of the metal. These investigators were able to state that the presence of no more than $\frac{1}{1000}$ of a milligram of the potassium salt is sufficient to give to the flame the characteristic spectrum of the element. By similar methods, the delicacy of the tests for lithium carbonate and sodium chlorate were shown to be a thousand times and three thousand times as delicate respectively. Practically, the detection of lithium and sodium spectroscopically is extremely easy and satisfactory, the only difficulty being that the exceeding delicacy of the sodium test, and the ubiquitousness of sodium salts often make a decision doubtful as to whether that element is present essentially in the substance under examination, or by accident. With potassium the case is different, and experience shows that, when the test is to be made for very small amounts of potassium, the simple method in vogue for developing the luminosity of lithium and sodium — the dipping of a single loop of platinum wire in the liquid or solid substance, and the placing of the loop in the Bunsen flame — fails, because, as it seems to us, so great a proportion of the material is dispersed before the heat of the flame effects the dissociation of the metal which precedes the production of the spectrum.

* From Am. Jour. Sci., xlii, 448.

We have endeavored to improve the conditions of exposure of the test-substance by making use of more powerful flames and by substituting for the single loop the hollow coils of platinum wire first recommended, so far as has come to our knowledge, by Truchot* in the description of a method for the quantitative determination of lithium. Such coils are easily made by winding the wire somewhat obliquely about a rod of suitable size, pressing the coils close together, and gathering the free ends into a twisted handle. The size of the coils is adjustable without difficulty, so that each coil may be made to hold almost exactly any appropriate amount, and to take up this amount with very little variation in successive fillings, provided only that the precaution be taken in the process of filling to plunge the coil while hot into the liquid, and to keep its axis inclined obliquely to the surface of the liquid while withdrawing it. How closely the capacity of such coils may be adjusted and how uniformly they may be filled is shown in the figures of the accompanying record.

	I.	II.	III.	IV.	V.	VI.
	grm.	grm.	grm.	grm.	grm.	grm.
Weight of filled coil. . . .	0.1996	0.2780	0.2794	0.2844	0.3572	0.3296
" "	0.1996	0.2780	0.2794	0.2845	0.3571	0.3296
" "	0.1996	0.2780	0.2794	0.2844	0.3572	0.3298
" "	0.1996	0.2780	0.2794	0.2845	0.3571	0.3298
" "	0.1996	0.2781	0.2794	0.2844	0.3571	0.3296
" empty coil . . .	0.1986	0.2760	0.2764	0.2804	0.3521	0.3100
" contents (mean)	0.0010	0.00202	0.0030	0.00404	0.00504	0.01968

It is plain that we have in these coils simple means of taking up known amounts of material in solution; and by gentle heating the liquid may be evaporated and the solid material left thinly and uniformly spread, not easily detachable, and so in condition to be acted upon with effect when brought to the flame. The evaporation may be conducted with little danger of loss of material by holding the handle of the coil across the flame with the coil proper at a safe distance outside; but we have generally, and preferably, used a hot radiator, over which

* Compt. rend., lxxviii, 1022.

the coils are exposed, the handles resting upon a flat asbestos ring. The burner which we have used in heating the coils before the spectroscope is of the Muencke pattern and gives a powerful flame 3 cm. wide at its base. We have generally adjusted the flame to a height of 20 cm., and have introduced the coil, after thorough drying, just within the outer mantle, on the side next the spectroscope, with the axis transverse to the slit of the spectroscope and the handle across the body of the flame. In cleaning the coils we have found it convenient to heat them in the flame of an Argand burner of the Fletcher pattern, beneath which is burned, in a small lamp, alcohol containing about a twentieth of its volume of chloroform. The products of combustion of the alcohol and chloroform are conveyed to the interior of the flame above by a glass funnel fitted by a cork to the tube of the Argand burner. This arrangement of apparatus gives a hot colorless flame through which hydrochloric acid is constantly diffused in condition to clean the wires completely and without attention. The spectroscope which we have employed is a well-made single prism instrument provided with a scale, and a movable observing telescope so that different portions of the spectrum may be viewed or cut off at will. The slit is adjustable, but for measuring its width we have been obliged to have recourse to the device of closing it upon wires of known gauge. Our work has been done in the ordinary diffused light of the laboratory, care having been taken to cut off from the room direct sunlight only; but in observing it has been our custom to shield the eye in use as completely as possible with the hand or with a dark handkerchief, and to cover the eye not in use. We have found it desirable to use the scale of the instrument, illuminated to the lowest degree of visibility, to aid the eye in placing barely visible lines.

Upon experimenting with the apparatus described, it was found that the largest coil used was best adapted to our purpose, and, accordingly, in all the experiments made subsequently, and recorded in the following account, coils holding $\frac{1}{50}$ of a gram of water, measuring 2 mm. in diameter by 1 cm.

in length, made of No. 28 wire (0.32 mm. in diameter), and wound in about thirty turns, were the ones employed. With these coils and the flame adjusted to a height of 20 cm. we have been able to recognise the presence of potassium, taken in the form of the chloride, in a coil-full of liquid containing 0.00066 grm. of the metal in 10 cm³, when the slit had a width of 0.18 mm.; and containing 0.0005 grm. in the same volume of solution when the slit was set 0.23 mm. wide. That is to say, $\frac{1}{1500}$ mg. of potassium to the coil-full produces a line distinctly visible with a slit of 0.18 mm., and $\frac{1}{2000}$ mg. with a slit of 0.23 mm., and it is evident that this practical method of producing the spectrum of potassium gives results of a delicacy approaching that indicated in the experiments of Bunsen and Kirchhoff.

These determinations were made with pure potassium chloride carefully prepared from the chlorate, but in practical analysis it almost always happens that sodium is also present. Experiments were therefore made to determine the influence of varying amounts of the latter upon the visibility of the

Weight of K in a coil-full.	Weight of Na in a coil-full.	Ratio of Na : K.	Width of slit.	Number of trials.	Characteristic of line.
mg.	mg.		mm.		
0.0010	0.0000	0 : 1	0.23	3	Visible.
0.0010	0.0020	2 : 1	0.23	3	Visible.
0.0010	0.0100	10 : 1	0.23	3	Visible.
0.0010	0.0200	20 : 1	0.23	3	Visible.
0.0010	0.0490	49 : 1	0.23	3	Visible.
0.0010	0.0500	50 : 1	0.23	4	Very faint or none.
0.0010	0.1000	100 : 1	0.23	3	None.
0.0010	0.2000	200 : 1	0.23	3	None.
0.0014	0.0000	0 : 1	0.18	3	Visible.
0.0014	0.0500	49 : 1	0.18	3	Visible.
0.0014	0.0700	50 : 1	0.18	3	Visible.
0.0014	0.1400	100 : 1	0.18	2	Visible.
0.0014	0.1400	100 : 1	0.18	2	None.

potassium line. The dilution of the potassium chloride was adjusted nearly to the last limit of visibility, so that a coil-full of the liquid should contain $\frac{1}{1500}$ mg., or $\frac{1}{2000}$ mg. of the element, according as the slit was 0.18 mm. or 0.23 mm. wide;

to this solution were added weighed amounts of pure sodium chloride twice reprecipitated and washed by hydrochloric acid; and the spectroscopic tests were carried out as before, the sodium line being kept within the field of view with the potassium line.

It is obvious from these results that a considerable amount of sodium may be present in the flame, when the sodium line is in full view in the spectrum, and the slit adjusted to nearly the lowest limit of visibility of pure potassium, without interfering with the appearance of the potassium line, but that a quantity of sodium amounting to a hundred times that of the potassium is sufficient to entirely overpower the spectrum of the potassium. The inference is plain that the proportion of sodium to potassium should not be permitted to reach 100 : 1 when it is desirable to bring out the full delicacy of the spectroscopic test with the sodium line in the field of view. When too great a proportion of sodium is present, its influence may be moderated by throwing the sodium line out of view, if the instrument in use possesses the necessary adjustment; otherwise, it is easy to effect a partial separation of the sodium chloride from the potassium chloride, before bringing the solution to the test, by precipitating with alcohol. Our experience shows that the delicacy of the test for potassium is not impaired materially by such treatment of the mixed chlorides. We found, for example, that 0.0070 grm. of potassium chloride mixed with 0.5 grm. of pure sodium chloride, dissolved in the least amount of water, and extracted carefully by about 7 cm^3 of absolute alcohol applied in successive portions, was so completely retained in solution and separated from sodium, that a coil-full taken from the solution diluted to 140 cm^3 gave the spectroscopic test for potassium distinctly with the slit at 0.23 mm. In this case, at least, the treatment did not diminish the delicacy of the test; for, a coil-full of the diluted solution could not have contained more than $\frac{1}{1000}$ mg. of potassium, if nothing had been lost. It was found, in like manner, that, by taking pains to evaporate the alcoholic extract, and to dissolve the residue in a drop of water, 0.0001

grm. of potassium originally present as the chloride with 0.5 grm. of sodium chloride, was easily found. By turning the observing telescope so as to cut off as completely as possible the sodium light we were able to detect potassium in four successive tests of a drop of the final solution which was just large enough to fill the coil four times, when the original amount of potassium present with 0.5 grm. of sodium chloride was 0.00001 grm. This is equivalent to detecting $\frac{1}{400}$ mg. of potassium in a drop large enough to fill the coil once. We were assured of the entire absence of potassium from the sodium chloride which we used by the fact that the similar extraction of 1 grm. of the salt by alcohol left a residue which yielded no line of potassium when examined spectroscopically. It is perhaps worth noting in passing that the coil may be made to pick up a drop of a size only sufficient to fill it by simply touching the coil while hissing hot to the drop.

Certain experiments in which the method of manipulation which we have described was applied to the determination of potassium salts other than the chloride indicated that the test is less delicate in the case of the sulphate, and rather more delicate in the case of the carbonate. We were able to find the red line of potassium unmistakably, when only $\frac{1}{2000}$ of a milligram of potassium was introduced into the flame in the form of the carbonate.

The quantitative determination of potassium by the spectroscope has never, so far as we know, been accomplished heretofore. Sodium appears to have been successfully estimated by Champion, Pellet, and Grenier* by the use of comparison flames, produced by the aid of complex mechanism, and a spectrophotometer of original construction. Lithium has been determined more simply, Truchot† having been the first to suggest a method of manipulation which was modified by Ballmann‡ and taken up later by Bell§ apparently without knowledge of the previous work on the same line. Truchot's method consists in comparing the duration and strength of the

* Compt. rend., lxxvi, 707.
† Compt. rend., lxxviii, 1022.
‡ Zeitschr. anal. Chem., xiv, 297.
§ Am. Chem. Jour., vii. 35.

spectral lines developed by exposure to the Bunsen flame of portions taken up in a platinum loop from the test-solution and standard solutions of different strengths. No analytical proofs of the value of the method were given and accuracy was not claimed beyond the recognition of differences of from three to four milligrams in a liter of liquid when amounts not exceeding forty milligrams per liter were compared. Ballmann discards as valueless the observation of the duration of the spectral line, advocates the dilution of the test and standard solutions to the absolute extinction of the line and employs hollow cones, measuring 2.5 mm. by 3.5 mm., to carry the liquids to the flame. Bell follows Ballmann's method of diluting the solutions to be compared to a common condition, but takes the vanishing point of the line instead of the point of absolute invisibility and makes his loops of platinum very small. Both Ballmann and Bell were able to estimate thallium similarly, but neither determined potassium, Bell declaring specifically that the method is inapplicable to the handling of that element.

Our success in determining potassium qualitatively by the use of powerful flames and coils of large dimensions was such as to encourage the attempt to apply quantitatively the same method of manipulating; and from certain preliminary experiments looking in this direction we found it best, for our purpose at least, to fall back upon Truchot's method of comparing visible lines, rather than to try to fix the vanishing point or the point of extinction of the spectral line. We chose a dilution of the standard solution which corresponds to the presence of $\frac{1}{500}$ mg. of potassium to the coil-full, and set the slit at a width of 0.23 mm., having found it most advantageous to work with lines for comparison bright enough to be visible without much effort. Our mode of proceeding is to dilute the test-solution until the line given by the potassium contained in a coil-full is of the same brightness as that given by the same quantity of the standard solution. From the final volume of the test-solution the quantity of potassium present in it is directly calculable; for, since any given volume of the test-

solution at its final dilution contains exactly the same amount of potassium as the same volume of the standard solution, we have only to multiply the number expressing the volume in cubic centimeters of the test-solution by the weight in grams of the potassium contained in one cubic centimeter of the standard in order to obtain the weight in grams of potassium in the whole test-solution. We found it convenient to use several coils adjusted to the same capacity, and to clean, fill, dry, and ignite them before the spectroscope in the manner previously described. From time to time the capacity of the coils should be readjusted, or else the final comparison tests should be made with a single coil. It is essential that the eye of the observer should be kept as nearly as possible in the same condition of sensitiveness and in the same position in making the comparisons, and to accomplish this end we found it best to hold the eye at the observing telescope during the entire interval between the exposures, to shade it carefully by the hand, or otherwise, to cover the eye not in use, to cut off all direct sunlight from the work-table (though the diffused light of the room is not objectionable), and to light the comparison scale of the spectroscope to the faintest possible visibility in order to fix exactly the position in which the line is to be sought. It is important, too, that the trials of the test and standard should come as closely together as possible in point of time. The observations of a series should be made by the same individual, the preparation and exposure of the wires being made by another. It is not possible to attain the best results in such work single-handed. The dilution of the test-solution is made conveniently, and with sufficient accuracy, in 100 cm^3 cylinders graduated to half cubic centimeters, the mixture being made thorough by passing the solution from vessel to vessel. It is often advantageous to divide a liquid which is to be diluted and to work with aliquot portions, so that it may be possible to retrace a step without trouble in case a portion of the solution has been unwittingly diluted too much; such a mode of proceeding is, of course, necessary when the final dilution must exceed 100 cm^3, unless large graduates are called into use.

Excepting the cases of very concentrated solutions, no significant loss of material is occasioned by the filling of the coils, the error thus introduced being trivial in comparison with that inherent in all photometric processes. The following is the record of our experience in the comparison of solutions of pure potassium chloride, the strength of the test-solution being unknown to the observer.

EXPERIMENT I.

Volume of test-solution.	Characteristic of line compared with standard.
cm³	
20	Stronger.
50	Stronger.
100	Stronger.
110	Stronger.
120	Stronger.
150	Like.
200	Weaker.
160	Weaker.
150	Like.
(150 × 0.0001 = 0.0150)	
	grm.
Potassium found . . .	0.0150
" taken . . .	0.0150
Limits on either side	0.0120
	0.0160
Error	0.0000

EXPERIMENT II.

Volume of test-solution.	Characteristic of line compared with standard.
cm³	
30	Stronger.
60	Stronger.
82	Weaker.
70	Stronger.
76	Stronger.
78	Stronger.
80	Like.
(80 × 0.0001 = 0.0080)	
Potassium found . . .	0.0080
" taken . . .	0.0080
Limits on either side	0.0078
	0.0082
Error	0.0000

These results show a degree of accuracy in the process quite unexpected. In the former no attempt was made to approximate as closely as possible to the limits of dilution on both sides of the condition of equal brightness in test and standard, but in the latter great care was taken in this respect and the possible error cannot exceed two and a half per cent of the entire amount of potassium involved.

Experiment III was made to discover the effect of the presence of a reasonable amount of sodium chloride upon the determination of the potassium. To a portion of the solution

of pure potassium chloride containing 0.01 grm. of the element was added 0.1 grm. of sodium chloride taken from the salt purified as previously described. This solution was diluted and the comparison made with the standard according to the accompanying account.

EXPERIMENT III.

Volume of the test-solution.	Characteristic of line compared with standard.
cm^3	
25	Stronger.
50	Stronger.
80	Stronger.
90	Stronger.
95	Stronger.
105	Stronger.
120	Like.

$(120 \times 0.0001 = 0.0120)$

	gr.
Potassium found	0.0120
" taken	0.0100
Error	0.0020

The result of this experiment was most surprising; for, instead of diminishing the delicacy of the test we find that the presence of a moderate amount of sodium chloride tends to increase the brilliance of the potassium line. The sodium chloride employed was a part of that prepared and tested as previously described and used in the experiments upon the qualitative determination of potassium. By no possibility could the 0.1 grm. of it taken in the experiment have contained more than 0.000001 grm. of potassium. It is evident, therefore, that the brilliance of the potassium line gained twenty per cent in strength by the influence of sodium chloride amounting to ten times the weight of the potassium present when the effect due to impurity of the salt could by no means exceed a hundredth of one per cent; that is to say, the observed effect is, at the very least two thousand times greater than that which might have been conceivably produced by contamination of the sodium salt.

In the following experiment the effect of varying amounts of sodium chloride upon the spectrum of the potassium is shown. The sodium line was turned out of the field of view to obviate the dazzling effect of the sodium light, and a solution of potassium chloride containing 0.01 grm. of the element in 100 cm^3 was examined spectroscopically after the addition of successively increasing amounts of sodium chloride, the strength of the line observed being brought into comparison with that produced by similar portions of the potassium solution containing no sodium.

Sodium chloride in a coil-full.	Potassium in a coil-full.	Ratio of NaCl : K.	Width of slit.	Characteristic of line compared with standard containing no NaCl.
mg.	mg.		mm.	
0.002	0.002	1 : 1	0.18	Like.
0.010	0.002	5 : 1	0.18	Like.
0.020	0.002	10 : 1	0.18	A little stronger.
0.040	0.002	20 : 1	0.23	Much stronger.
0.200	0.002	100 : 1	0.23	Very much stronger.
0.400	0.002	200 : 1	0.23	Much stronger.
0.600	0.002	300 : 1	0.23	Much stronger.

From this it appears that the maximum strengthening effect occurs when the sodium chloride stands to the potassium in the ratio of 100 : 1. The apparent diminution of brilliance when the sodium is increased beyond that proportion is doubtless due to the effect of the strong light diffused through the field of view by the intensely bright sodium flame in spite of the fact that the line itself is cut off from direct vision.

The cause of the brightening effect of the sodium chloride we are inclined to attribute to the chemical action of the sodium dissociated in the flame. The effect of ammonium chloride, and of hydrochloric acid, in destroying the potassium light is well known, and is due, presumably, in very large degree to the prevention of the dissociation of the potassium chloride. The dissociated sodium should, naturally by its mass-action reinforce the disintegrating action of the heat upon the molecule of potassium chloride.

It is plain that the complication introduced into the quantitative spectroscopic determination of potassium by the presence of the sodium salt in the test can be obviated if it can be brought about that both the test and the standard solution shall contain the same amount of that reagent. It is a matter of interest, therefore, to discover whether it is possible to match sodium lines of considerable intensity so closely that the quantities of that element in solutions brought into comparison shall be practically equal, and so may be relied upon to give the same strengthening effect to the potassium spectrum. The following statement is the record of an attempt in this direction. The narrower slit was found to be best adapted to the comparison of the sodium lines,

NaCl in a coil-full of new solution.	NaCl in a coil-full of standard.	Width of slit.	Characteristic of line as compared with that of standard.
mg.	mg.	mm.	
0.010	0.02	0.18	Weaker.
0.017	0.02	0.18	Weaker.
0.019	0.02	0.18	Weaker.
0.020	0.02	0.18	Like.

The result shows the possibility of matching the sodium lines with a degree of approximation sufficient for the purpose in view; and, accordingly, a new standard solution was made containing 0.01 grm. of potassium taken in the form of the chloride and 0.1 grm. of sodium chloride in 100 cm^3 and with this new standard the following determinations were made. The experiment was performed in three stages: first, the test-solution was diluted until its potassium line matched approximately with that of the standard; secondly sodium chloride was added to the solution thus diluted until the sodium lines were brought to equality; and finally, the test-solution and the standard were again brought into comparison.

EXPERIMENT IV.

Part I.			Part II.			Part III.		
Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.	NaCl in 100 cm³ of test-solution.	Width of slit.	Characteristic of sodium line as compared with standard.	Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.
cm³	mm.		grm.	mm.		cm³	mm.	
80	0.23	Stronger.	0.01*	0.18	Weaker.	108	0.28	Weaker.
70	0.23	Stronger.	0.03	0.18	Weaker.	108	0.23	Stronger.
100	0.23	Weaker.	0.05	0.18	Weaker.			Weaker.
			0.08	0.18	Weaker.	109	0.28	Stronger.
			0.09	0.18	Weaker.			Like.
			0.10	0 18	Like.			

The test-solution having been accidentally over-diluted, its strength was increased by the addition of 0.0010 grm. of potassium and this amount was added in the computation below to that originally in the test-solution.

$(109 \times 0.0001 = 0.0109)$

Potassium found . . . 0.0109 grm.
" taken . . . 0.0110 "
Error . . . . . 0.0001 " = 0.9 per cent.

EXPERIMENT V.

Part I.			Part II.			Part III.		
Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.	NaCl in 100 cm³ of test-solution.	Width of slit.	Characteristic of sodium line as compared with standard.	Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.
cm³	mm.		grm.	mm.		cm³	mm.	
40	0.23	Stronger.	0.025*	0.18	Weaker.	160	0.23	Stronger.
100	0.23	Stronger.	0.050	0.18	Weaker.	180	0.23	Stronger.
160	0.23	Weaker.	0.085	0.18	Weaker.	190	0.23	Stronger.
			0.100	0.18	Weaker.	200	0.23	Stronger.
			0.110	0.18	Like.	205	0.23	Weaker.
						210	0.23	Weaker.

$(205 \times 0.0001 = 0.0205$
$200 \times 0.0001 = 0.0200\}$ mean $= 0.02025)$

Potassium found . . . . . 0.02025 grm.
" taken . . . . . 0.02000 "
Error . . . . . 0.00025 " = 1.25 per cent.

* Originally present.

EXPERIMENT VI.

Part I.			Part II.			Part III.		
Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.	NaCl in 100 cm³ of test-solution.	Width of slit.	Characteristic of sodium line as compared with standard.	Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.
cm³	mm.		grm.	mm.		cm³	mm.	
40	0.23	Stronger.	0.045*	0.18	Weaker.	110	0.23	Stronger.
80	0.23	Stronger.	0.082	0.18	Like.	120	0.23	Stronger.
100	0.23	Stronger.				130	0.23	Like.
110	0.23	Like.						

$(130 \times 0.0001 = 0.0130)$

Potassium found . . . . 0.0130 grm.
" taken . . . . 0.0140 "
Error . . . . . 0.0010 " = 7 per cent.

EXPERIMENT VII.

Part I.			Part II.			Part III.		
Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.	NaCl in 100 cm³ of test-solution.	Width of slit.	Characteristic of sodium line as compared with standard.	Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.
cm³	mm.		grm.	mm.		**First.**		
80	0.23	Stronger.	0.05*	0.18	Weaker.	cm³	mm.	
90	0.23	Stronger.	0.07	0.80	Weaker.	100	0.23	Stronger.
100	0.23	Weaker. Like.	0.09	0.18	Weaker.	120	0.23	Stronger.
			0.10	0.18	Like. Stronger. Stronger.	130	0.23	Stronger.
						140	0.23	Stronger. Weaker.
						Second.		
						cm³	mm.	
						120	0.23	Stronger.
						140	0.23	Stronger.
						150	0.23	Stronger. Weaker.
						160	0.23	Weaker.

First.		Second.	
$(140 \times 0.0001 = 0.0140)$		$(150 \times 0.0001 = 0.0150)$	
Potassium found .	0.0140 grm.	. . . . .	0.0150
" taken .	0.0150 "	. . . . .	0.0150
Error	0.0010 " = 7 per cent	. . . . .	0.0000

* Originally present.

From these results it is plain that the sodium in test and standard may be matched closely enough to allow a fair approximation to be made in the determination of the potassium. In Experiments IV, V and VI, no readjustment of the percentage of sodium in the final dilution, subsequent to the matching of the sodium lines, was attempted; in Experiment VII this point was looked to, so that in this determination the strength of the sodium was kept equal to that found in the matching process. In Experiments IV and VII, the matching of the sodium in the test-solution against that in the standard proved to have been exact; in V, an excess of 10 per cent was added, and in VI, the point of equality was thought to have been reached while there was still a deficiency of 25 per cent in the sodium chloride of the test-solution.

The error in the determination of the potassium in Experiment VI may, perhaps, be accounted for by the mistake in matching the sodium; that of the first attempt in Experiment VII, we are disposed to attribute to lack of care in keeping the eye of the observer in the most sensitive condition, and of attention to the point of bringing the wires to the plane in quick succession. The largest absolute error met with amounted to one milligram in a total of fifteen. Though not accurate to the last degree when large amounts of potassium are to be estimated, the method, we think, offers some advantage without too great sacrifice of exactness in the determination of small amounts. In qualitative work the mode of manipulating described is exceedingly satisfactory. Aside from the practical application of the method the point which has been of greatest interest to us is the development of the fact that the presence of sodium salts in the flame is of direct influence in strengthening the spectrum of potassium.

XIII

A METHOD FOR THE QUANTITATIVE SEPARATION OF STRONTIUM FROM CALCIUM BY THE ACTION OF AMYL ALCOHOL ON THE NITRATES.

By P. E. BROWNING.*

FOLLOWING the general procedure laid down in the Gooch process for the separation of sodium and potassium from lithium by the action of amyl alcohol on the chlorides, I undertook a series of experiments looking toward the separation of strontium from calcium by the action of amyl alcohol on the nitrates. On boiling several portions of the so-called chemically pure calcium and strontium nitrates with amyl alcohol, nearly complete solubility was observed in case of the calcium salt, while corresponding insolubility seemed to be characteristic of the strontium salt, and these results seemed to warrant proceeding with the work.

For the quantitative tests to be described standard solutions of specially purified strontium and calcium nitrates were prepared. In general the preparation was effected by precipitating a soluble salt of either element with ammonium carbonate in the presence of ammonium chloride, washing thoroughly with boiling water, dissolving in the least possible amount of nitric acid, and making up to measure. In the earlier experiments other methods of purification were used, such as the precipitation of the strontium nitrate by alcohol, and in case of the calcium salt the preparation of the nitrate from the carbonate precipitated by ammonium carbonate from a solution of calcium sulphate. The method first described, however, gave satisfactory results, the spec-

* From Am. Jour. Sci., xliii, 50.

troscope failing to show in the product thus obtained any trace of intermixture of calcium and strontium salts, or the presence of any other appreciable impurity. In the determination of the standards of these solutions definite amounts were drawn off from burettes into counterpoised beakers or crucibles (according as the method of determination was by precipitation or evaporation) and weighed as a check on the burette reading. The strontium nitrate in each portion was converted into the sulphate either by precipitation in the presence of alcohol, or by evaporating and igniting, these methods yielding results closely agreeing. The calcium was determined by evaporation with sulphuric acid. The first series of experiments was directed toward an investigation of the action of amyl alcohol upon strontium nitrate alone. Accordingly several amounts of the strontium salt were measured from a burette into counterpoised Bohemian beakers of about 100 cm^3 capacity, and weighed. The water was then evaporated over a water bath, and the dry salts dissolved in a few drops of water and boiled with 30 cm^3 of amyl alcohol, that amount being determined upon for convenience. Care should be taken not to add more than the necessary amount of water to dissolve the salt, inasmuch as the presence of much water delays the process (it being necessary to expel all the water before the amyl alcohol can do its work) and tends to cause spattering due to the superheating of the water and consequent sudden generation of steam under the alcohol. It has been my experience that in the presence of a few drops of water the boiling goes on quietly, the water escaping easily through the amyl alcohol, so that in the course of a few minutes the alcohol reaches its normal boiling temperature (128°–130°C.). In order that the inflammable fumes of the alcohol might not reach the flame during the boiling the beaker was placed upon a piece of asbestos board about 15 cm. square. When the temperature of the alcohol reached its normal boiling point (128°–130° C.), as shown by a thermometer, the beaker was removed and the strontium nitrate filtered off upon an asbestos felt in a perforated plati-

num crucible, the crucible and felt having been previously dried and weighed.

The filtration was carried on under gentle pressure, the filtrate being received in a beaker standing under a bell jar upon a ground glass plate. The last traces of strontium nitrate were removed from the beaker by washing with small amounts of previously boiled amyl alcohol contained in a wash-bottle, the mouthpiece of which consisted of a small chloride of calcium tube passing through the stopper and drawn out and plugged at the lower end with cotton to exclude particles of the calcium salt from the alcohol. By this device the introduction of moisture into the amyl alcohol was guarded against. The crucible containing the strontium nitrate was placed in an air bath and heated to 150° C. to drive off all amyl alcohol, and weighed. A constant weight was obtained uniformly in one treatment. Series I contains the results of these experiments, the strontium being calculated as oxide.

SERIES I.

Exp.	SrO taken.	SrO found.	Loss.
	grm.	grm.	grm.
(1)	0.1229	0.1220	0.0009
(2)	0.1231	0.1221	0.0010
(3)	0.1230	0.1219	0.0011
(4)	0.1227	0.1213	0.0014

These results suggested a possible solubility of the strontium salt, and, accordingly, experiments were made to test this point. Amounts of strontium nitrate closely agreeing with those above were taken and treated in the same manner. The filtrates amounting, without the washings, to about 25 cm^3 were evaporated to dryness. The residue was ignited to burn off organic matter from the amyl alcohol, treated with sulphuric acid, heated to low redness, and weighed. In two cases the residue of strontium sulphate was found to contain of the oxide respectively 0.0009 grm. and 0.0010 grm. As will be seen, the solubility of the strontium nitrate aver-

ages about 0.0010 grm. of the oxide to 30 cm³ of amyl alcohol used. The exact extent of this solubility depends, of course, upon the amount of amyl alcohol remaining after boiling; and, since the source of heat is removed as soon as the normal boiling temperature of the alcohol is reached, very little decrease in the volume of the previously boiled alcohol results. On measuring the amounts of the alcohol remaining in several experiments I found them to approximate closely to 25 cm³. It seemed justifiable, therefore, to add as a correction to the apparent amount of strontium oxide found 0.0010 grm. for every 25 cm³ of amyl alcohol remaining, or for every 30 cm³ originally taken. Experiments were also made to determine whether the strontium nitrate might have been at all broken down in the process of boiling and heating so that some strontium might be present in the final residue in the form of oxide or nitrite. In two of these experiments portions of strontium nitrate left by the treatment with amyl alcohol were dissolved, precipitated as the sulphate and weighed as such, and the results of these experiments (5) and (6) go to show that the composition of the strontium nitrate is not appreciably changed in the process of separation and drying. In certain other experiments directed to the same end, the residues of the process of separation were, after weighing and drying, treated with a drop of nitric acid, and again dried at 150° C. and weighed. These tests (7) and (8) confirm the indications of the previous experiments. Finally a third experiment was made upon strontium nitrate dried at 150° C. to see what decomposition might result by heating to temperatures somewhat higher than 150° C. — the temperature at which the residues of the previous experiments had been dried. The result shows that the loss in the twenty-five degrees above 150° C. is exceedingly slight.

Exp. (5)	$Sr(NO_3)_2$ calculated as SrO	0.1219 grm.
	The same dissolved and precipitated as $SrSO_4$ calculated as SrO	0.1219 grm.

Exp. (6)	$Sr(NO_3)_2$ calculated as SrO	0.1213 grm.
	The same dissolved and precipitated as $SrSO_4$ calculated as SrO	0.1214 grm.
(7)	$Sr(NO_3)_2$ calculated as SrO	0.1228 grm.
	The same dried at 150° C. after adding a drop of HNO_3	0.1228 grm.
(8)	$Sr(NO_3)_2$ calculated as SrO	0.1239 grm.
	The same dried at 150° C. after adding a drop of HNO_3	0.1239 grm.
(9)	Weight of $Sr(NO_3)_2$ dried at 150° C. . . .	0.2482 grm.
	Weight of the same portion dried at 165° C.	0.2480 grm.
	Weight of the same portion dried at 175° C.	0.2478 grm.

When calcium nitrate was treated in a similar manner by boiling with amyl alcohol the mass of the salt dissolved, but minute portions separated out on the bottom or sides of the beaker. Such residues were, however, very small and on weighing were found not to exceed 0.0003 grm. or 0.0004 grm. of the oxide. In several instances this insoluble residue was washed thoroughly with ethyl alcohol, dissolved in water, tested before the spectroscope and found to give the characteristic calcium spectrum. All experience pointed to the fact that the formation of the residue was due to some very slight change of composition of the calcium nitrate. On one or two occasions the acidified solution of the residue appeared to reduce a drop of an extremely dilute solution of potassium permanganate, and this action suggested the presence of a nitrite. Treatment of this residue with nitric acid and subsequent evaporation of the excess of acid failed, however, to leave the calcium salt in a condition to be dissolved by amyl alcohol.

It is possible, therefore, that the real cause of insolubility is to be sought in the oxidation of the amyl alcohol and consequent formation of an organic acid, and, subsequently, of the corresponding calcium salt, but the amounts of the residue were so extremely small that it was not practicable to

solve this question, at once, exactly and satisfactorily without directing attention too far from the main issue. Moreover, the error introduced by this peculiar behavior of the calcium salt proved to be insignificant in its effects upon the quantitative determination of the calcium, and accordingly, it was disregarded in the subsequent tests.

The next experiments were directed toward a separation of strontium and calcium nitrates. Definite amounts of a solution of strontium nitrate were measured from burettes into counterpoised beakers and weighed, as already described, the calcium nitrate was then added in solution, and the weight taken again. The water was evaporated and the dry salts dissolved again in the least possible amount of water, and boiled with amyl alcohol (30 cm^3) as before. The strontium salt was filtered off into a perforated platinum crucible containing an asbestos felt, dried and weighed as previously described. The calcium was determined in the form of the sulphate, by evaporation of the alcohol, treatment with an excess of sulphuric acid, and ignition.

Correction was made for the solubility of the strontium nitrate, and its consequent presence with the calcium, by calculating the amount dissolved in the portion of amyl alcohol employed to the condition of sulphate and subtracting that quantity from the apparent amount of calcium sulphate found. The results of this mode of proceeding are recorded in experiments (10) and (11).

Exp.	SrO taken.	SrO found (corrected).	Error.	CaO taken.	CaO found (corrected).	Error.
	grm.	grm.	grm.	grm.	grm.	grm.
(10)	0.0911	0.0932	0.0021+	0.0932	0.0907	0.0025−
(11)	0.0915	0.0945	0.0030+	0.0933	0.0899	0.0034−

After making the correction in the manner specified it is evident that the amount of strontium indicated is greater than that originally taken. It is apparent, therefore, that the strontium nitrate must have been contaminated, probably

mechanically, by the calcium salt, as the calcium salt is found to be correspondingly deficient in amount. It was thought best, therefore, to have recourse to a double treatment with the alcohol. Accordingly after the first boiling already described the alcohol carrying the greater part of the calcium in solution was decanted upon an asbestos felt under the conditions previously described and collected in a beaker placed to receive it. The residue was then dried at a gentle heat over a radiator to remove amyl alcohol, dissolved in a few drops of water, treated with a drop of nitric acid to assure the condition of nitrate, and evaporated to dryness. After dissolving in a few drops of water 30 cm^3 of the alcohol were added, and the boiling repeated. The residue was filtered off upon the same felt through which the first portion had been decanted, and washed with amyl alcohol, care being taken to remove all particles of the residue from the beaker by careful rubbing. The crucible and residue were heated in an air bath at 150° C. as before, and then weighed. The filtrate from the two treatments and the washings were treated differently in two series of experiments. In Series II, the filtrate was precipitated with sulphuric acid, ethyl alcohol being added to secure thorough mixture. The precipitated sulphate was filtered off upon asbestos, heated to low redness and weighed. In Series III, the alcoholic filtrate was evaporated to a small volume, transferred to a weighed platinum crucible and evaporated. The residue was ignited to burn off organic matter, treated with sulphuric acid and again ignited at low redness and weighed.

SERIES II.

Exp.	SrO taken.	SrO found (corrected).	Error.	CaO taken.	CaO found (corrected).	Error.
	grm.	grm.	grm.	grm.	grm.	grm.
(12)	0.1235	0.1239	.0004+	0.1290	0.1271	0.0019−
(13)	0.1237	0.1228	.0009−	0.1246	0.1226	0.0020−
(14)	0.1239	0.1239	.0000	0.1248	0.1223	0.0025−
(15)	0.1974	0.1972	.0002−	0.0502	0.0492	0.0010−
(16)	0.1979	0.1978	.0001−	0.0496	0.0482	0.0014−

SERIES III.

Exp.	SrO taken.	SrO found (corrected).	Error.	CaO taken.	CaO found (corrected).	Error.
	grm.	grm.	grm.	grm.	grm.	grm.
(17)	0.0148	0.0155	0.0007+	0.0256	0.0254	0.0002—
(18)	0.0183	0.0183	0.0000	0.1030	0.1015	0.0015—
(19)	0.0364	0.0366	0.0002+	0.0516	0.0511	0.0002—
(20)	0.0365	0.0365	0.0000	0.0515	0.0513	0.0002—
(21)	0.0493	0.0494	0.0001+	0.0515	0.0502	0.0013—
(22)	0.0497	0.0497	0.0000	0.0519	0.0511	0.0008—
(23)	0.0497	0.0503	0.0006+	0.0249	0.0245	0.0004—
(24)	0.0729	0.0732	0.0003+	0.0257	0.0251	0.0006—
(25)	0.0730	0.0732	0.0002+	0.0255	0.0255	0.0000
(26)	0.0744	0.0744	0.0000	0.0258	0.0260	0.0002+
(27)	0.0912	0.0910	0.0002—	0.1286	0.1276	0.0010—

The average error in the determination of strontium in both series is less than 0.0001 grm. + on the oxide; that of the calcium amounts to 0.0017 grm. — on the oxide in Series II, and to 0.0005 grm. — in Series III.

In both processes the correction for the solubility of strontium nitrate in amyl alcohol, determined as previously described, was applied — 0.0020 grm. being added to the weight of the strontium oxide found after the double treatment with amyl alcohol, and 0.0035 grm. being deducted from the apparent weight of the calcium sulphate found before calculating it to the form of the oxide. The latter of the two processes, which are identical so far as handling of the strontium is concerned, yields the better results in the determination of the calcium, doubtless because a trifling amount of calcium sulphate remains in solution in the final filtrate in the former process, while in the latter every trace should be recovered. The deposition of minute traces of calcium in the precipitation of the strontium nitrate, to which reference has been previously made, is evidently a matter of no significance in comparison with the ordinary errors of manipulation.

More recent work * has demonstrated the possibility of using very much smaller amounts of amyl alcohol in the boiling than the amounts formerly used (30 cm^3 for each

* Am. Jour. Sci., xliv, 462.

treatment). By the use of smaller beakers (50 cm^3 capacity) 10 cm^3 of the alcohol can be conveniently substituted for 30 cm^3, and the correction for solubility of the strontium nitrate is thus reduced from 0.001 grm. on the oxide to 0.0003 grm. in each treatment, and the corresponding amount of sulphate to be substracted from the calcium sulphate before calculating to the condition of oxide is reduced from 0.0017 grm. to 0.0005 grm. in each treatment. The necessity of a double treatment, or the use of two portions of 10 cm^3 each of the alcohol, brings the total correction to 0.0006 grm. on the strontium oxide, and 0.0010 on the calcium as sulphate. For ordinary work such a correction may be disregarded. The following tables give the corrected and uncorrected results.

TABLE I (correction disregarded).

Exp.	SrO taken.	SrO found.	Error.	CaO taken.	CaO found.	Error.
	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.0570	0.0565	0.0005—	0.0534	0.0540	0.0006+
(2)	0.0573	0.0567	0.0006—	0.0534	0.0543	0.0009+
(3)	0.0285	0.0274	0.0011—	0.0272	0.0276	0.0004+
(4)	0.0568	0.0560	0.0008—	0.0535	0.0537	0.0002+
(5)	0.0568	0.0561	0.0007—	0.0533	0.0535	0.0002+
(6)	0.0288	0.0280	0.0008—	0.0271	0.0272	0.0001+
(7)	0.1420	0.1416	0.0004—	0.0535	0.0544	0.0009+
(8)	0.1419	0.1416	0.0003—	0.0665	0.0669	0.0004+
(9)	0.1135	0.1132	0.0003—	0.1066	0.1070	0.0004+
(10)	0.1137	0.1126	0.0011—	0.1064	0.1070	0.0006+

TABLE II (correction applied).

Exp.	SrO taken.	SrO found (corrected).	Error.	CaO taken.	CaO found (corrected).	Error.
	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.0570	0.0571	0.0001+	0.0534	0.0536	0.0002+
(2)	0.0573	0.0573	0.0000	0.0534	0.0539	0.0005+
(3)	0.0285	0.0280	0.0005—	0.0272	0.0272	0.0000
(4)	0.0568	0.0566	0.0002—	0.0535	0.0533	0.0002—
(5)	0.0568	0.0567	0.0001—	0.0533	0.0531	0.0002—
(6)	0.0288	0.0286	0.0002—	0.0271	0.0268	0.0003—
(7)	0.1420	0.1422	0.0002+	0.0535	0.0540	0.0005+
(8)	0.1419	0.1422	0.0003+	0.0665	0.0665	0.0000
(9)	0.1135	0.1138	0.0003+	0.1066	0.1066	0.0000
(10)	0.1137	0.1132	0.0005—	0.1064	0.1066	0.0002+

XIV

A METHOD FOR THE QUANTITATIVE SEPARATION OF BARIUM FROM CALCIUM BY THE ACTION OF AMYL ALCOHOL ON THE NITRATES.

By P. E. BROWNING.*

The fact that strontium can be separated quantitatively from calcium by boiling the nitrates with amyl alcohol, as I have recently shown, † naturally suggested a similar separation of barium from calcium by the same general treatment. Solutions of specially purified barium and calcium nitrates were prepared and standardized, either by the evaporation or filtration of definite portions after treatment with sulphuric acid. The mean of several closely agreeing results, both by evaporation and filtration, was taken as the standard. The method followed was essentially the same as described in the method for the quantitative separation of strontium from calcium referred to above. The first series of experiments was directed toward an investigation of the action of amyl alcohol upon barium nitrate alone. Accordingly definite amounts of the barium salt were measured into Bohemian beakers of about 100 cm^3 capacity and weighed. The water was then evaporated over a water bath, and the dry salts dissolved in a few drops of water and boiled with 30 cm^3 of amyl alcohol, that amount being determined upon as convenient, until the normal boiling point of the alcohol was reached — 128° to 130° C. During the boiling the beaker was placed upon a piece of asbestos board about 15 cm. square to keep the inflammable fumes of the alcohol from the flame. When the temperature of the alcohol reached its normal boiling point

* From Am. Jour. Sci., xliii, 314.

† Am. Jour. Sci., xliii, 50. This volume, p. 107.

the beaker was removed and the barium nitrate filtered off upon an asbestos felt in a perforated platinum crucible, the crucible and felt having been previously dried and weighed. The filtration was carried on under gentle pressure, the filtrate being received in a beaker standing under a bell jar upon a ground glass plate. The last traces of barium nitrate were removed from the beaker by washing with small amounts of anhydrous amyl alcohol contained in a wash bottle, previously described, to the mouth piece of which a small chloride of calcium tube was connected. The crucible containing the barium nitrate was placed in an air bath and heated to 150° C. The process of heating and weighing was repeated until a constant weight was obtained. Series I shows the results of these experiments the barium being calculated as oxide.

SERIES I.

Exp.	BaO taken.	BaO found.	Error.
	grm.	grm.	grm.
(1)	0.1040	0.1039	0.0001–
(2)	0.1043	0.1043	0.0000
(3)	0.0524	0.0522	0.0002–
(4)	0.0519	0.0518	0.0001–

These results show plainly enough the complete insolubility of the barium salt in the amyl alcohol; but to confirm them the filtrates of (3) and (4) were evaporated to dryness, ignited to burn off any organic matter from the amyl alcohol, treated with sulphuric acid, heated to low redness and weighed. The weights in both cases showed the absence of any residue.

SERIES II.

Exp.	BaO taken.	BaO found.	Error.	CaO taken.	CaO found.	Error.
	grm.	grm.	grm.	grm.	grm.	grm.
(5)	0.1410	0.1406	0.0004 –	0.0112	0.0114	0.0002 +
(6)	0.1300	0.1301	0.0001 +	0.0926	0.0926	0.0000
(7)	0.1043	0.1049	0.0006 +	0.0741	0.0736	0.0005 –
(8)	0.0781	0.0781	0.0000	0.0556	0.0554	0.0002 –
(9)	0.0525	0.0526	0.0001 +	0.0373	0.0372	0.0001 –

SERIES III.

Exp.	BaO taken.	BaO found.	Error.	CaO taken.	CaO found.	Error.
	grm.	grm.	grm.	grm.	grm.	grm.
(10)	0.1304	0.1308	0.0004 +	0.0927	0.0921	0.0006 −
(11)	0.1043	0.1046	0.0003 +	0.0371	0.0370	0.0001 −
(12)	0.1037	0.1036	0.0001 −	0.0743	0.0744	0.0001 +
(13)	0.0783	0.0776	0.0007 −	0.0427	0.0422	0.0005 −
(14)	0.0519	0.0521	0.0002 +	0.0369	0.0361	0.0008 −
(15)	0.0519	0.0512	0.0007 −	0.0570	0.0567	0.0003 −
(16)	0.0261	0.0259	0.0002 −	0.0925	0.0925	0.0000

The next experiments were directed toward a separation of barium and calcium nitrates. Definite amounts of a solution of barium nitrate were measured from burettes into counterpoised beakers and weighed, as already described, the calcium nitrate was then added in solution and the weight taken again. The water was evaporated and the dry salts dissolved again in the least possible amount of water, and boiled as before with 30 cm^3 of amyl alcohol. The barium salt was filtered off into a perforated platinum crucible containing an asbestos felt, dried and weighed as previously described. The calcium was determined in the filtrate, in the form of the sulphate, by evaporation of the alcohol, treatment with an excess of sulphuric acid and ignition. Series II gives the results of this treatment.

In Series III the effect of a double treatment with the alcohol is recorded. In these experiments, after the first boiling, already described, the alcohol was decanted upon an asbestos felt, under the conditions previously mentioned, and collected in a beaker placed to receive it. The residue was then dried at a gentle heat over a radiator to remove amyl alcohol, dissolved in a few drops of water, and this solution was treated with a drop of dilute nitric acid to assure the condition of nitrate, and evaporated to dryness. After dissolving in a few drops of water, 30 cm^3 of alcohol were added, and the boiling repeated. The residue was filtered off upon the felt through which the first portion had been decanted and washed with amyl alcohol, care being taken to remove all particles from the

beaker by careful rubbing. The crucible and residue were heated to 150° C. as before and weighed. The results after one treatment are fully as satisfactory as those after the double treatment, — a point which simplifies the method considerably. In the separation of strontium from calcium the double treatment was necessary. The form in which the salts separate suggested a possible explanation. The strontium nitrate separates in plate-like masses, while the barium is much more granular and therefore less liable to include foreign matter.

SERIES IV.

Exp.	$Ba(NO_3)_2$ and $Sr(NO_3)_2$ taken.	$Ba(NO_3)_2$ and $Sr(NO_3)_2$ found and corrected.	Error in nitrates.	Error averaged and calculated as oxide.	CaO taken.	CaO found.	Error.
	grm.	grm.	grm.	grm.	grm.	grm.	grm.
(17)	0.3941	0.3945	0.0004+	0.0002+	0.0283	0.0277	0.0006—
(18)	0.1436	0.1442	0.0006+	0.0003+	0.0568	0.0558	0.0010—
(19)	0.3163	0.3152	0.0011—	0.0006—	0.0284	0.0274	0.0010—
(20)	0.1978	0.1987	0.0009+	0.0005+	0.0285	0.0280	0.0005—
(21)	0.1948	0.1932	0.0016—	0.0008—	0.0833	0.0835	0.0002+
(22)	0.1971	0.1971	0.0000	0.0000	0.0830	0.0817	0.0013—
(23)	0.1973	0.1960	0.0013—	0.0007—	0.0830	0.0824	0.0006—
(24)	0.1959	0.1970	0.0011+	0.0005+	0.0830	0.0819	0.0011—
(25)	0.1971	0.1963	0.0008+	0.0004+	0.0834	0.0831	0.0003—

Series IV contains the results of certain experiments directed toward the separation of barium and strontium together from calcium. Definite portions of the three nitrate solutions were measured into counterpoised beakers and the successive weights taken as previously described. The method of treatment was the same as that described in the double treatment of the barium and calcium salts. The correction for the solubility of the strontium salt was applied (0.001 grm. of strontium oxide to 30 cm^3 of the alcohol used) in the manner defined in the paper upon the separation of strontium from calcium. The results are tabulated for the nitrates in the cases in which barium and strontium were treated together, but the errors are also averaged on the oxides for the amounts of barium and strontium nitrates

taken in order that they may be compared more conveniently with the results of the previous series.

In Experiments (21) and (25) 15 cm^3 of the alcohol were used in each boiling instead of the 30 cm^3 of the previous experiments, and thus the total amount of the corrections for the solubility of the strontium salt was reduced one-half. In Experiments (21), (23) and (25) the calcium was determined by precipitation with sulphuric acid, the precipitate being filtered off, ignited at low redness and weighed.

The rapidity of execution and satisfactory character of the results of this method of separating barium from calcium seem to place it among good analytical methods.

XV

ON THE QUALITATIVE SEPARATION AND DETECTION OF STRONTIUM AND CALCIUM BY THE ACTION OF AMYL ALCOHOL ON THE NITRATES.

By P. E. BROWNING.*

In a recent paper† I have shown that strontium and calcium may be separated quantitatively by boiling the nitrates of these elements with amyl alcohol and applying the corrections determined for the solubility of the strontium salt. The qualitative separation, however, is somewhat vitiated by the deposition of a slight residue upon the bottom of the test-tube or beaker when calcium nitrate is boiled with amyl alcohol. While this deposit weighs but a few tenths of a milligram and is insignificant in its effect upon the interpretation of the quantitative results, it may easily be mistaken for strontium in the qualitative test unless tested spectroscopically. This residue when dried, dissolved in water and nitric acid, and again treated with amyl alcohol is not dissolved completely but again separates out wholly or partially. The possibility of the formation of the calcium salt of an organic acid by the action of the nitric acid on the amyl alcohol (a point to which reference was made in the paper before mentioned), suggested the idea that ignition might so change the residue that it would not reappear upon a second boiling with the amyl alcohol. Experiment proved the truth of this presumption; for it was found that after getting the ignited residue into solution with water and a drop of dilute nitric acid, subsequent boiling with amyl alcohol effected complete solution, as shown by experiments (1), (2), (3), (4) of Series I below.

* From Am. Jour. Sci., xliii, 386.

† Am. Jour. Sci., xliii, 50. This volume, p. 107.

In applying the method qualitatively, small amounts of the amyl alcohol may be conveniently used and the boiling carried on in a test-tube, care being taken to keep the inflammable fumes of the alcohol from the flame. Five cubic centimeters of the alcohol is a convenient amount to use in each boiling and the error introduced by the solubility of the strontium salt is thus reduced to a minimum, the solubility in 30 cm^3 having been determined to be 0.001 grm. of the oxide. Experiments made to test the delicacy of the method as regards the detection of strontium alone are recorded in Series I (5), (6), (7), (8), (9); and (10), (11), (12), (13) give the results of the treatment in the presence of both strontium and calcium. Into a test-tube is put the mixture of the nitrates of strontium and calcium not exceeding 0.2 grm., that being the limit of the solubility of calcium nitrate in 5 cm^3 of amyl alcohol. After dissolving in a few drops of water, 5 cm^3 of amyl alcohol are added and the boiling is carried on until the normal boiling point of the alcohol, 128–130° C., is reached. If strontium is present to the amount of 0.001 grm. of the oxide or more a very decided separation takes place. If the amount is smaller it cannot be readily distinguished from the residual spots deposited on the bottom of the tube by the calcium salt. The alcohol containing the calcium salt dissolved is decanted upon a dry filter paper in a dry funnel and the residue washed in the tube with about 5 cm^3 of absolute ethyl alcohol, this also being filtered into the tube containing the amyl alcohol. The filtrate is reserved to be tested for calcium, while the residue, if so small that it may be a calcium deposit, is dried gently and finally ignited by agitating the tube over a flame. After cooling the tube a few drops of water and a drop of nitric acid are added and the boiling repeated. As the results of Series I show, any amount of strontium above 0.0005 grm. of the oxide separates out distinctly, while the slight calcium residue does not reappear. My experience has been that amounts of calcium nitrate equal to 0.2 grm. give a deposit on the first boiling about equal to 0.0003 grm. of strontium oxide on the first boiling. The

residues from the second treatment in Series I (5) to (13) were all dissolved in a few drops of water treated with a drop of hydrochloric acid and tested before the spectroscope, all giving distinct strontium lines but no trace of calcium. The calcium residues from the first boiling gave distinct calcium lines but no trace of strontium.

SERIES I.

Exp.	SrO taken.	$Ca(NO_3)_2$ taken.	Deposit after first boiling.	Deposit after second boiling.
	grm.	grm.		
(1)	. . .	0.1	Trace.	None.
(2)	. . .	0.2	Slight.	None.
(3)	. . .	0.2	Slight.	None.
(4)	. . .	0.2	Distinct.	Faintest trace.
(5)	0.0003	. . .	Faint trace.	Faint trace.
(6)	0.0003	. . .	Faint trace.	Faintest trace.
(7)	0.0005	. . .	Distinct.	Distinct.
(8)	0.0005	. . .	Distinct.	Distinct.
(9)	0.0010	. . .	Distinct.	Distinct.
(10)	0.0010	0.2	Distinct.	Distinct.
(11)	0.0005	0.1	Distinct.	Faintest trace.
(12)	0.0007	0.1	Distinct.	Faint trace.
(13)	0.0008	0.05	Distinct.	Distinct.

SERIES II.

Exp.	$Sr(NO_3)_2$ taken.	CaO taken.	Result.
	gr.	grm.	
(1)	0.001	. . .	Faint granular cloudiness.
(2)	0.1	. . .	" " "
(3)	0.2	. . .	" " "
(4)	. . .	0.001	Decided flocky floating masses.
(5)	. . .	0.0005	" " " "
(6)	. . .	0.0002	" " " "
(7)	. . .	0.0001	Plain " " "
(8)	. . .	0.00005	Faint " " "
(9)	0.1	0.0005	Decided " " "
(10)	0.1	0.0002	" " " "
(11)	0.1	0.0001	Plain " " "
(12)	0.2	0.0002	Decided " " "

The delicacy of the process in the detection of calcium is shown by the experiments of Series II. The method of treatment was the same as described above excepting that the

filtrates and washings after the first boiling were used for these tests. To these clear filtrates about 2 cm^3 of dilute sulphuric acid were added, and in five minutes or less the results recorded were apparent. When strontium alone was taken either in large or small amounts, the result was uniformly a faint cloudiness gathering after standing some time to a minute precipitate of a granular character. In the case of the calcium the detection could be carried easily to 0.0005 grm. of the oxide, and satisfactory results were obtained with 0.0002 grm. The character of the precipitate in the case of calcium was, moreover, distinctive, it being in every case light and flocky, and collecting in floating masses. With the precautions noted very satisfactory results can be obtained by this method, not the least advantage being the rapidity with which a determination can be made. It will be noticed that in some cases calcium and strontium are recorded as the nitrates and in others tabulated as oxides. When either strontium or calcium were used in large quantities the pure nitrate was weighed out directly; when very small amounts were used these were taken from the standardized solutions of the nitrates used in the quantitative work, the standards of which had been recorded in terms of the oxide. The strontium and calcium salts used in this work were specially purified by the methods detailed in my previous paper.

XVI

A METHOD FOR THE DETERMINATION OF BARIUM IN THE PRESENCE OF CALCIUM AND MAGNESIUM.

By F. W. MAR.*

THE recent investigation† by R. Fresenius of the value of the various methods which have been proposed for the separation of barium and calcium, shows that but two of the methods tested by him are sufficiently accurate for good analytical work, and even with these it is necessary to make two treatments in order to obtain a complete separation. The method here described may therefore be of interest and by reason of its rapidity and accuracy may prove valuable, although since the publication of the work of Fresenius another method‡ has been published from this laboratory which, in point of accuracy, leaves little to be desired.

It has long been known that barium chloride is insoluble to a marked degree in concentrated hydrochloric acid, but the difficulty of filtering off the strong acid has in the past prevented the determination of the exact amount of this insolubility, and for the same reason the reaction has not been available for quantitative use. Since the invention of the Gooch crucible, however, the treatment of such strong acid filtrates has become a matter of the greatest ease, and it seemed worth while to investigate the limits of the insolubility of barium chloride in the strong acid and to ascertain whether the reaction might not be of use in the separation of

* From Am. Jour. Sci., xliii, 521.

† Zeitschr. anal. Chem., xxx, 595.

‡ Browning: Am. Jour. Sci., xliii, 314. This volume, p. 116.

barium from calcium and magnesium, the chlorides of which are soluble in the strong acid.

The barium chloride used in the following experiments was the pure crystallized chloride containing two molecules of water. The calcium salt was the pure fused chloride, and the magnesium salt was the pure crystallized magnesium chloride dried at 50° C. As the two latter were not determined in the experiments it was not necessary to know the composition of the salts used as regards hygroscopic moisture. Attention was first given to determining the solubility of barium chloride in hydrochloric acid.

SERIES A.

Exp.	$BaCl_2 . 2H_2O$.	Water.	HCl.	Total filtrate.	$BaCl_2$.	Loss.
	grm.	cm³	cm³	cm³	grm.	grm.
(1)	0.5024	5	20	. . .	0.4241	0.0041
(2)	0.5084	5	20	. . .	0.4304	0.0030
(3)	0.5099	2	25	. . .	0.4320	0.0027
(4)	0.5033	2	25	90	0.4251	0.0039
(5)	0.5047	2	25	52	0.4247	0.0055
(6)	0.5065	2	50	115	0.4257	0.0060
(7)	0.5008	2	50	75	0.4218	0.0051
(8)	0.5011	2	50	93	0.4220	0.0051
(9)	0.5024	2	75	123	0.4246	0.0037

The experiments in Series A were made as follows: — The barium salt was weighed out, placed in a small beaker and dissolved in the amount of water indicated. The barium was then precipitated as the anhydrous chloride by adding, gradually at first, the amount of hydrochloric acid shown. After standing for five or ten minutes the precipitates were filtered off upon asbestos in Gooch crucibles, washed with concentrated hydrochloric acid, dried sometimes over a low flame (at about 150°–200° C.) and sometimes in an air bath heated to 165° C. and weighed. In several cases the total filtrate was measured and the volume is given in the tabular statement. The results show a considerable solubility amounting to about 1 part in 8000 under the conditions given.

SERIES B.

Exp.	$BaCl_2 . 2H_2O$.	Water.	HCl.	Total filtrate.	$BaCl_2$.	Loss.
	grm.	cm^3	cm^3	cm^3	grm.	grm.
(10)	0.5057	2	25	75	0.4268	0.0042
(11)	0.5017	5	50	90	0.4198	0.0078
(12)	0.5068	3	50	100	0.4285	0.0085
(13)	0.5019	2	100	144	0.4186	0.0082

The experiments in Series B were conducted similarly to those of Series A except that the precipitates were allowed to stand 24 hours before filtration. The loss due to solubility was, as is shown by the table, greater than before, due doubtless to the escape of hydrochloric acid gas from the solution.

SERIES C.

Exp.	$BaCl_2 . 2H_2O$.	Water.	HCl.	Alcohol.	$BaCl_2$.	Loss.
	grm.	cm^3	cm^3	cm^3	grm.	grm.
(14)	0.5011	3	25	15	0.4228	0.0043
(15)	0.5096	2	25	10	0.4278	0.0066

The experiments of Series C were conducted in the same manner as those of Series A except that the amount of absolute alcohol indicated was added after the precipitation by hydrochloric acid. The results show that the alcohol neither decreased nor increased the amount of the solubility of the chloride.

SERIES D.

Exp.	$BaCl_2 . 2H_2O$.	HCl.	$BaCl_2$.	Loss.
	grm.	cm^3	grm.	grm.
(16)	0.5019	50	0.4249	0.0029
(17)	0.5020	50	0.4257	0.0022
(18)	0.5020	50	0.4255	0.0024
(19)	0.5016	50	0.4259	0.0017
(20)	0.5022	50	0.4267	0.0014

In the experiments of Series D the weighed barium chloride was placed in an Erlenmeyer beaker and dissolved in

four or five cubic centimeters of water. The indicated amount of acid was then added, and a stream of hydrochloric acid gas was passed for two hours into the cooled mixture. The precipitates were then treated as in the former experiments. The results show that even in the strongest possible solution, at the ordinary temperature, of hydrochloric acid barium chloride is soluble to a considerable degree, this solubility amounting according to the first three experiments of the series to about one part in 20,000. In Exp. 18 and 19 ten cubic centimeters of absolute ether were added to the solution before passing in the hydrochloric acid gas. The results showed that the ether seemed to decrease the solubility of the barium salt, and therefore the experiments of the following series were undertaken.

SERIES E.

Exp.	$BaCl_2 . 2H_2O$.	HCl.	Ether.	$BaCl_2$.	Loss.
	grm.	cm^3	cm^3	grm.	grm.
(21)	0.5008	50	10	0.4267	0.0002
(22)	0.5002	50	10	0.4257	0.0007
(23)	0.4999	50	10	0.4252	0.0009
(24)	0.4999	50	10	0.4258	0.0003
(25)	0.5003	25	25	0.4259	0.0005
(26)	0.5002	25	5	0.4262	0.0002
(27)	0.5099	25	5	0.4344	0.0003
(28)	0.5003	25	5	0.4261	0.0003

The experiments of Series E were conducted as follows. The amount of barium salt specified was dissolved in the least, convenient, amount of hot water (about 2 cm^3) and precipitation was brought about by adding the indicated amount of concentrated hydrochloric acid. The beaker containing the precipitate was then placed in cold water and the amount of ether shown in the tables was added and mixed with the solution by thorough stirring. After standing for five or ten minutes the precipitate was filtered off and washed with concentrated hydrochloric acid containing about ten per centum by volume of absolute ether and dried, sometimes in an air bath at 165°–175° C. and at others over a radiator

giving a temperature of 175°–200° C. A constant weight was more quickly obtained by the latter method and it was used exclusively in the experiments of the subsequent series. In using it a low heat was used at first and the temperature was not increased until the precipitate was moderately dry. The results show that barium chloride is practically insoluble in a mixture of hydrochloric acid and ether containing about one-sixth by volume of the latter. The average solubility calculated from the experiments given is one part in 122,000. The actual solubility is less than this since no account was taken of the volume of the washings which were at least equal to the original filtrates.

SERIES F.

Exp.	$BaCl_2 . 2H_2O$.	$CaCl_2$.	HCl.	Ether.	$BaCl_2$.	Loss.
	grm.	grm.	cm^3	cm^3	grm.	grm.
(29)	0.5001	0.5	50	10	0.4250	0.0013
(30)	0.4999	0.5	50	10	0.4250	0.0011
(31)	0.5005	0.5	25	25	0.4260	0.0006
(32)	0.5002	0.42	25	5	0.4258	0.0004
(33)	0.5001	0.5	25	5	0.4255	0.0008
(34)	0.5005	0.5	25	5	0.4251	0,0015
(35)	0.5001	0.5	25	5	0.4254	0.0009
(36)	0.5001	0.5	25	5	0.4258	0.0005
(37)	0.5003	0.5	25	5	0.4261	0.0004
(38)	0.1002	3.0	25	5	0.0842	0.0010
(39)	0.0107	3.0	25	5	0.0080	0.0005
(40)	0.5100	0.5	25	. .	0.4328	0.0020

Series F was undertaken to test whether the mode of precipitating barium used in the preceding series would be of use in the separation of the barium from calcium. The experiments were conducted as in Series E, except that the calcium salt was dissolved with the barium chloride. It was necessary to use more water than in Series E to effect solution, but as the barium salt was uniformly the last to dissolve the effect was practically the same as before. The results show that mixtures of barium and calcium in all proportions are perfectly separated by this method, 0.010 grm. of barium chloride being separated with accuracy from 3 grm. of calcium chloride. The calcium does not show the slight-

est tendency to come down with the barium, and those experiments in which separation was effected by the use of 25 cm³ of hydrochloric acid and 5 cm³ of ether gave rather better results than those in which double this volume was employed. It is better not to let the precipitations stand too long before filtration, even if kept cold, as the hydrochloric acid evaporates from the solutions, and experiments in which filtration was delayed for about two hours (e. g., Exps. 33, 34, 35) show a rather larger loss than the average. That there is no advantage in increasing the amount of ether over the proportions used above is shown by Exp. 31, which is comparable with Exp. 25. In the case of Exp. 40, in which no ether was used, the result is comparable with the experiments of Series A. The precipitate was washed, however, with the mixture of hydrochloric acid and ether.

SERIES G.

Exp.	$BaCl_2 . 2H_2O$.	$MgCl_2 . 6HO_2$.	HCl.	Ether.	$BaCl_2$.	Loss.
	grm.	grm.	cm³	cm³	grm.	grm.
(41)	0.4999	0.5	25	5	0.4253	0.0007
(42)	0.5000	0.5	25	5	0.4257	0.0005
(43)	0.1002	3.0	25	5	0.0844	0.0008
(44)	0.0100	3.0	25	5	0.0077	0.0008

The experiments of Series G were made in exactly the same manner as those of Series F, except that varying amounts of magnesium chloride were present instead of the calcium salt. The results are uniform and exact, and indicate that barium may be separated from magnesium when the two are present in any proportion. It is probable that if magnesium chloride were present in an amount larger than 3 grm. in 30 cm³ it would be necessary to make two treatments, as under those circumstances it shows a slight tendency to precipitate. The amount of mixed salts present should always, therefore, be kept below this limit.

Recapitulation. — Barium chloride is soluble to an extent not exceeding one part in 20,000 in pure concentrated hydro-

chloric acid, but the solubility increases very rapidly with the diminution in the strength of the acid. In concentrated hydrochloric acid containing ether it is soluble to an amount not exceeding one part in about 120,000. To utilize this fact for the separation of barium from calcium and magnesium the chlorides of the earths are dissolved in the least possible amount of boiling water and precipitated by 25 cm^3 of concentrated hydrochloric acid with the addition of 5 cm^3 of absolute ether after cooling. The acid should be added drop by drop at first allowing the precipitate formed to redissolve as long as possible, as the precipitate is thus obtained in a coarse crystalline condition and filters very quickly and is less liable to include foreign matter. After standing a few minutes the precipitate is to be filtered in a Gooch crucible, washed with hydrochloric acid containing about 10 per cent of ether and dried at 150°–200° C. The method is accurate and rapid, and possesses the further advantage when a number of determinations are to be made that the precipitate may be dissolved off the felt by a little water and, after ignition, the crucible and felt may be used again without reweighing. A felt upon which half a dozen precipitates were weighed did not change its weight to the extent of one-tenth of a milligram. The fumes of the strong acid cause no inconvenience if the filtration is performed in front of a good flue. A gas flame may be used in the flue without danger from the ether which seems to be firmly held by the hydrochloric acid. A flame was used to increase the draught in all of the experiments given and with entire safety, even when the filtrate contained 50 per cent by volume of ether.

XVII

A METHOD FOR THE IODOMETRIC DETERMINATION OF NITRATES.

By F. A. GOOCH and H. W. GRUENER.*

It has been shown by DeKoninck and Nihoul † that nitrates may be decomposed completely by the prolonged action of gaseous hydrochloric acid, and determined with accuracy by measuring the iodine set free when the products of decomposition, carefully kept from atmospheric contamination, act upon potassium iodide. These investigators recognized the difficulties attending the use of gaseous hydrochloric acid in analytical processes, and endeavored unsuccessfully to substitute the strong aqueous solution for the gaseous acid. The work to be described in the following account was performed in the search for a simpler method for the iodometric determination of nitrates.

According to a process recently developed in this laboratory, ‡ chloric acid may be determined with the greatest ease. It was shown that in the interaction of a chlorate with potassium iodide, arsenic acid, and sulphuric acid, in regulated quantities in aqueous solution and at the boiling temperature, the first action of the hydriodic acid set free from the iodide by the sulphuric acid is upon the chloric acid, and that not until this action is completed is the arsenic acid attacked and reduced with the simultaneous liberation of a corresponding amount of iodine. If the arsenic acid is taken in quantity sufficient to insure the final decomposition of the entire amount of iodide present, the arsenious acid found at

* From Am. Jour. Sci., xliv, 117.

† Zeitschr. angew. Chem., 1890, 477.

‡ Gooch and Smith, Am. Jour. Sci., xlii, 220, this volume, p. 83.

chlorine of the higher chlorides is evolved and manganous chloride remains. During the process of heating the color of the solution passes from the original characteristic green through darker shades to black and returns by the reverse changes to the original tint. The decomposition of the nitrate extends under the conditions to the last traces, but the breaking up of the nitrates with the formation of the higher chloride, does not take place completely in the presence of water amounting to more than a third of the volume of the solution, and an action already established in strong acid is reversed by the addition of a large amount of water. Chlorates, peroxides, and other substances which liberate oxygen or chlorine when in contact with strong hydrochloric acid induce similar phenomena, but in the absence of such other substances the reaction serves to detect nitrates when present in fairly small amounts (perhaps one part in sixty thousand) as shown in the accompanying table:

KNO_3 taken.	$MnCl_2 \cdot 4H_2O$ in strong HCl.	Color developed.
grm.	cm^3	
0.01000	10	Black.
0.00500	5	Black.
0.00100	5	Dark brown.
0.00050	5	Dark green.
0.00025	5	Deepened tint.
0.00015	5	Deepened tint.
0.00005	5	None.
0.00000	5	None.

In the first attempts to apply this reaction to the quantitative estimation of nitrates, 10 cm^3 of the manganous mixture, the pure weighed nitrate, and an excess of potassium iodide were put in a tubulated retort fitted with a hollow ground stopper drawn out at both ends so as to serve for the introduction of carbon dioxide evolved in a Kipp's generator charged with marble and acid previously boiled. The neck of the retort passed through a rubber stopper nearly to the bottom of a side-neck Erlenmeyer flask, used as a receiver,

in the mouth of which the stopper fitted tightly. The side-neck of the receiver was joined by a rubber connector with a bent glass tube passing through a rubber stopper and reaching nearly to the bottom of a side-neck test tube into the mouth of which the stopper was fitted.

The first receiver contained hydrogen sodium carbonate in excess of the amount needed to neutralize the acid in the retort as it should distil over, a considerable quantity of potassium iodide (about 3 grm.) to aid in dissolving condensed iodine, and arsenious oxide in known amount and in excess of the quantity necessary to convert to hydriodic acid the free iodine evolved. The second smaller receiver was partly filled with a dilute solution of potassium iodide and hydrogen sodium carbonate. The current of carbon dioxide was started immediately upon introducing the contents of the retort, and the air was safely removed before the darkening of color, which begins to appear very soon, had spread through the liquid. Heat was applied, and the evolution of nitric oxide and later that of iodine began. The distillation was continued until nearly all the liquid had passed over. Finally, the contents of both receivers were united and titrated against decinormal iodine. The difference between the excess of arsenious oxide remaining unoxidized and the amount originally present was taken as the measure of the iodine liberated and, accordingly, of the nitrate decomposed, upon the presumption that two molecules of the nitrate liberate ultimately six atoms of iodine according to the equation

$$2HNO_3 + 6H\text{-}I = 4H_2O + 2NO + 3I\text{-}I.$$

The choice of the solution for the retention of the halogen evolved was dictated by the consideration, in the first place, that very little iodine could pass through the alkaline arsenite to come into contact with the rubber stopper of the receiver on the way to the second absorbing liquid, and, secondly, that higher oxides of nitrogen reformed by the action of traces of air possibly introduced with the carbon dioxide or imperfectly

removed by it could not liberate iodine from an iodide in alkaline solution.

The iodide was introduced into the retort because, having chosen to collect the halogen in alkaline solution, it became necessary to take steps to break up, before it should reach the receiver, all nitrosyl chloride, the formation of which our experience in former lines of work not here detailed had led us to expect under the circumstances. In acid solution containing an iodide, nitrosyl chloride liberates iodine and is registered; in alkaline solution it breaks up with the formation of a chloride and a nitrite, the latter having no immediate action upon the arsenite. The results of experiments made in this manner are recorded in the accompanying table.

TABLE I.

KNO_3 taken.	KI in retort.	$MnCl_2$ mixture.	KNO_3 found.	Error.
grm.	grm.	cm^3	grm.	grm.
0.1036	0.8	10	0.1009	0.0027—
0.1083	0.8	10	0.1082	0.0001—
0.1064	0.8	10	0.1053	0.0011—
0.1068	0.8	10	0.1033	0.0035—
0.0551	0.8	10	0.0531	0.0020—

The experiments of Table II were carried out in a manner essentially similar to that of the experiments of Table I, excepting the single point that the iodine evolved in the

TABLE II.

KNO_3 taken.	KI in retort.	$MnCl_2$ mixture.	KNO_3 found.	Error.
grm.	grm.	cm^3	grm.	grm.
0.2039	1.6	20	0.2025	0.0014—
0.1060	0.8	10	0.1035	0.0025—
0.1036	0.8	10	0.1016	0.0020—
0.1013	0.8	10	0.1002	0.0011—
0.0521	0.5	10	0.0521	0.0000
0.0235	0.5	5	0.0227	0.0008—
0.0273	0.5	5	0.0262	0.0011—
0.0136	0.2	5	0.0132	0.0004—
0.0011	0.2	5	0.0009	0.0002—

possible under certain conditions of dilution, would account satisfactorily for the deficiency in the results of titration effected in alkaline solution. Upon this presumption the simple and obvious modification of titrating in acid solution should correct the error. Accordingly in the following series of experiments the plan of collecting the halogen and titrating in alkaline solution was abandoned, and since the addition of an iodide to the retort was no longer essential this practice was discontinued. The products of the action of the nitrate upon the manganese mixture — chlorine, nitric oxide and perhaps nitrosyl chloride, — were received directly in potassium iodide, and the iodine set free was titrated by sodium thiosulphate, itself standardized against iodine of known value with respect to a standard solution of decinormal arsenious oxide.

With the abandonment of the plan of putting the alkaline arsenite into the receiver the tendency of the iodine to pass onward to the second receiver is augmented and the possible action of the rubber stopper of the receiver becomes correspondingly dangerous. We modified the apparatus, therefore, so that only glass should occur where by any possibility rubber connections might act upon the free halogen. In place of the ordinary retort we adopted a form of apparatus made use of formerly by one of us in the quantitative distillation of boric acid under the action of methyl alcohol — a pipette bent and fitted as shown in the figure. To this apparatus was sealed a Varrentrapp and Will nitrogen bulb, the exit tube of which was drawn out so that it might be pushed well within the inlet tube of the second receiver — a Will and Varrentrapp absorption flask — and held in place by an outside rubber connector. The third receiver acts simply as a trap to exclude air from the absorption apparatus proper. In conducting the experiment the receivers were charged with solutions of potassium iodide, the first containing three grams, the second one gram, and the third only a fraction of a gram for every tenth of a gram of nitrate used. The first receiver was kept cool during the process by immersion in water. The intro-

duction of the nitrate and manganous mixture following it was made easy and safe by applying gentle suction to the end of the absorption train. The current of carbon dioxide was started immediately after putting in the manganous mixture, and after a suitable time had elapsed for the removal of air heat was applied to the retort and the distillation was continued until nearly all the liquid had passed over. Finally the contents of the receivers were united, the washing of the bulbs was effected easily and expeditiously by passing the wash-water directly through retort and receiver (the introduction of the manganese chloride into the distillate being not at all prejudicial to the accuracy of the titration), and the estimation of free iodine made by sodium thiosulphate as described. The results of the experiments conducted in this manner are given in Table III.

TABLE III.

KNO_3 taken.	$MnCl_2$ mixture.	KNO_3 found.	Error in terms of KNO_3.	Error in terms of HNO_3.
gm.	cm³	gm.	gm.	gm.
0.2038	20	0.2047	+0.0009	+0.0006
0.2062	20	0.2057	−0.0005	−0.0003
0.1082	10	0.1085	+0.0003	+0.0002
0.1017	10	0.1014	−0.0003	−0.0002
0.1040	10	0.1040	0.0000	0.0000
0.1027	10	0.1022	−0.0005	−0.0003
0.0526	10	0.0528	+0.0002	+0.0001
0.0513	10	0.0512	−0.0001	−0.0001
0.0254	10	0.0254	0.0000	0.0000
0.0252	10	0.0253	+0.0001	+0.0001
0.0507	5	0.0506	−0.0001	−0.0001
0.0512	5	0.0513	+0.0001	+0.0001
0.0255	5	0.0254	−0.0001	−0.0001
0.0252	5	0.0252	0.0000	0.0000
0.0254	5	0.0254	0.0000	0.0000
0.0253	5	0.0253	0.0000	0.0000

These results are fairly satisfactory. The mean error of the entire series is practically negligible. The maximum is quite not equal.

In view of the process which gives the basis for these results, namely the distillation of the nitrate of the nitric acid, a satisfactory

solution of crystallized manganous chloride in strong hydrochloric acid in an atmosphere of carbon dioxide, the passage of the products of action into potassium iodide, and the titration of the liberated iodine by sodium thiosulphate. It is important to take precautions to prevent the contact of the free halogen with rubber stoppers or connectors, and any apparatus, suitable for ordinary quantitative distillation and absorption, which meets this condition will probably answer the requirements of the process. Our own preference is for the apparatus described and figured.

The titration should be completed as soon as may be after admitting air to the distillate in order that traces of dissolved nitric oxide may not be reoxidized and again react upon the iodide present to liberate more iodine.

stand which students usually find unwieldy and difficult to dispose of in limited space. The brass fitting into which is cut a strong screw thread, as shown in Fig. 4, is set directly in the face of the work table with its upper surface flush with that of the table, and is held in place firmly by screws if the table-top is of wood, or by bolts and nuts if the table-top is of soapstone or other material which does not afford holding ground for ordinary screws. Iron rods of sizes and lengths suited to holding all sorts of apparatus, from the lighter forms used in elementary laboratory instruction to the heavier lecture apparatus, are cut with screws matching the thread of the brass fitting and may be set firmly in place as shown in the figures. The rods are of course interchangeable as occasion may require. When stripped of apparatus the rod takes up very little table space, but if a clear table is desired, it is easy to remove the rod by means of tongs kept at hand for the purpose in the laboratory tool-box. This device is neat, inexpensive, and easily made by any worker in brass and iron.

FIG. 4.

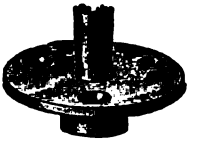


FIG. 5.

Steam Evaporator. — A convenient, simple, and inexpensive form of individual steam-bowl is easily constructed in the form shown in Fig. 6 wherever steam connections are available. An ordinary glass funnel of suitable size is hung in an iron ring, for holding which the rod support previously described serves admirably. The stem of the funnel is cut off short and a T-tube is attached as shown, set in a short piece of rubber tubing, with the lower end of the vertical branch bent to make a water-trap, while the horizontal branch is connected with the steam supply. A pipe to convey away the condensed water which overflows from the trap is a convenience, but in the

FIG. 6.

Funnels fitted with outlet tubes set in rubber stoppers, as shown in the figure, answer well for containing vessels, and the rod and socket device described above serves as a support for the apparatus. In the case of the particular apparatus which I have used the air was admitted to the atomizer under a pressure of about one-third of an atmosphere above the ordinary.

Certain experiments made to determine whether ferric chloride or chromic acid might be used in the purifier instead of dilute nitric acid showed that the superficial effect of these reagents upon the extremely finely comminuted mercury prevents the reunion of the particles even when submitted to considerable pressure. When dilute nitric acid is employed no such difficulty arises.

XIX

ON CERTAIN POINTS IN THE INTERACTION OF POTASSIUM PERMANGANATE AND SULPHURIC ACID.

By F. A. GOOCH and E. W. DANNER.*

In an article published some years ago by Jones † upon the action of reducing agents upon potassium permanganate the statement is made that in the interaction of oxalic acid and the permanganate in whatever way the conditions were varied — whether there was excess of oxalic acid or of permanganate, whether the solutions were strong or dilute, whether acid was present or not — in every case oxygen was obtained as a product of the reaction. The action between the permanganate and ferrous salts, in presence or absence of acids, in dilute or strong solutions, was said to yield oxygen similarly. In the discussion which followed the reading of this paper before the Chemical Society (London), some adverse comment seems to have been made.‡

More recently,§ in developing his excellent volumetric methods for the estimation of tellurium, Brauner has noticed a similar effect in the action of potassium permanganate upon tellurous oxide dissolved in sulphuric acid, and has shown, further, that in this particular case the evolution of oxygen is proportional to the amount of sulphuric acid employed, and that in working with alkaline solutions little evidence of such action appears.

The production of permanganic acid, and secondarily of free oxygen and ozone, by the action of strong sulphuric acid

* From the Am. Jour. Sci., xliv, 301.

† Jour. Chem. Soc., xxxiii, 95.

‡ Ber. Dtsch. chem. Ges., xi, 257.

§ Jour. Chem. Soc., lix, 238.

upon a permanganate is one of the commonest of phenomena, and the formation of a precipitate, consisting largely of hydrated manganese dioxide, by the action of hot dilute sulphuric acid upon the permanganate in aqueous solution is likewise well known. It seemed desirable to us, therefore, to study further the action of sulphuric acid of different strengths upon the permanganate in solution, with a view to determining how far such action may be responsible directly or indirectly for the liberation of free oxygen in oxidations brought about in the presence of the acid. In the first set of experiments directed to this end we determined the amount of potassium permanganate remaining after exposure to the action of sulphuric acid during different intervals of time and under varying conditions of strength and temperature. The permanganate was used in approximately decinormal solutions (3.16 grms. to the litre) the exact strength of which was determined relatively to an approximately decinormal solution of oxalic acid. In fixing the standard small portions (usually 10 cm^3) of the oxalic acid were diluted to a volume of 100 cm^3 by means of sulphuric acid of two per cent strength by volume, the solution was heated to 70° C. or 80° C., and the permanganate was added as usual until the first permanent blush of color appeared.

The general mode of proceeding in the test experiments was, in brief, to mix the solution of permanganate with the sulphuric acid (always previously diluted with an equal volume of water, and cooled) and, after the lapse of time indicated to add oxalic acid in quantity a little more than sufficient to bleach the entire amount of permanganate, warm to about 80° C., and titrate the residual oxalic acid by gradual addition of more permanganate. The difference between the amount of permanganate needed under the conditions to destroy the known amount of oxalic acid and that used in the determination of the standard should measure the oxygen lost by the permanganate under the action of the sulphuric acid. The results and details of these experiments are given below.

TABLE I.

H_2SO_4 [1 : 1].	Water.	$K_2Mn_2O_8$ in decinormal solution.	Percentage of H_2SO_4 [1 : 1] in solution during action.	Percentage of $KMnO_4$ used as compared with that required by theory.
		A. Treated immediately.		
cm³	cm³	cm³		
2	8	10	10	100
4	6	10	20	100
6	4	10	30	101.5
8	2	10	40	101.6
10	. .	10	50	101.9
		B. Treated after standing eight hours at ordinary temperature.		
2	8	10	10	99.7
4	6	10	20	99.7
6	4	10	30	101.3
8	2	10	40	105.3
10	. .	10	50	115.7
		C. Treated after standing five days at ordinary temperature.		
2	8	10	10	104
4	6	10	20	121.6
6	4	10	30	149.7
1	2	10	40	155.9
10	. .	10	50	156.4
		D. Treated after standing one and one-half hours at 80° — 90° C.		
2	8	10	10	101.3
4	6	10	20	143.8
6	4	10	30	135.9
8	2	10	40	149.1
10	. .	10	50	155.3

It is manifest from an inspection of Table I that the decomposition of the permanganate increases directly in each series of experiments with the increase in the proportion of sulphuric acid, that the amount of decomposition is greater as the time of action is extended, and that increase of temperature heightens the change. We note in particular, for example, that the presence of ten per cent of [1 : 1] sulphuric

acid induces at the ordinary temperature no immediate decomposition of the permanganate, none in eight hours, and a breaking down amounting to four per cent in five days; and that the presence of fifty per cent of acid of the same strength occasions the decomposition of about two per cent at once, fifteen per cent in eight hours, and more than half the entire amount of permanganate in the course of five days. It is evident also that twenty per cent of the [1 : 1] acid produces no appreciable effect at ordinary temperatures and under exposures of a few hours only. The effect of heating the mixture of acid and permanganate to 80° C. for an hour and a half is closely comparable with that brought about by the five days' action at the ordinary temperature.

In another series of similar experiments, the detailed record of which we omit as unnecessary, the absolute amounts of liquid and acid were increased while the proportion of the latter to the whole volume of the former was preserved. The volume of the liquid containing the acid and permanganate was fixed at 100 cm^3 and the absolute amounts of acid were taken five times as great as those used at corresponding points of the preceding series. The amounts of decomposition observed in these experiments followed those of the first series so closely as to compel the conclusion that it is the proportion of acid present rather than the absolute amount which is chiefly influential in the decomposition of the permanganate under given conditions. In still another series of experiments which differed from the last in the single point that the amount of permanganate used was increased fivefold, no appreciable differences in effect which might be traced to such extra use of permanganate were discoverable.

It is, of course, possible, and even probable, that some decomposition of the permanganate by the sulphuric acid might be brought about after the addition of the oxalic acid during the warming of the mixture up to the temperature at which the oxalic acid and permanganate interact. The experiments of Table II were therefore undertaken to test this point. In them oxalic acid was replaced by a solution

of ferrous sulphate in order to secure the removal of the residual permanganate at ordinary temperatures. The greatest care was taken to guard against atmospheric oxidation during the course of the experiment. The solution of ferrous sulphate was standardized before and after making the test experiments and found to be unchanged during the period of work. In the first five experiments of series B the proportions of acid and liquid of series A were preserved while the absolute volumes were increased; in the last four experiments the range of variation in proportions was extended.

TABLE II.

H_2SO_4 [1 : 1].	Water.	$KMnO_4$ in decinormal solution.	Percentage of H_2SO_4 [1 : 1] in solution during action.	Percentage of $KMnO_4$ used as compared with that required by theory.
		A. Treated at once.		
cm³	cm³	cm³		
2	8	10	10	100
4	6	10	20	100.2
6	4	10	30	100.1
8	2	10	40	100.1
10	..	10	50	100.3
		B. Treated at once.		
10	80	10	10	100.1
20	70	10	20	100.1
30	60	10	30	100
40	50	10	40	100.5
50	40	10	50	101.3
60	30	10	60	103
70	20	10	70	105
80	10	10	80	103.3
90	..	10	90	108.1

The results of these experiments indicate, as was anticipated, that rather less decomposition of permanganate is caused by the sulphuric acid when the reduction of the residual permanganate is effected at ordinary temperatures.

The increase in the amount of decomposition as the proportions of sulphuric acid [1 : 1] present are pushed beyond fifty per cent of the liquid is striking.

We have studied these same phenomena still further, varying, however, the mode of proceeding so as to observe and measure the gas evolved from the liquid as Jones* and Brauner* did in their individual investigations of the evolution of oxygen during oxidations. In these experiments tubes of suitable size and length, holding from 100 cm^3 to 200 cm^3, were sealed at one end, filled completely with the mixtures of acid and permanganate, inverted, and allowed to stand with the lower and open end submerged in liquid of the exact composition of that which filled them. The details and results of these experiments are recorded in Table III.

TABLE III.

Time elapsed.	A. H_2SO_4[1 : 1] = 50 per cent.		B. H_2SO_4[1 : 1] = 25 per cent.	
	Gas from 100 cm^3	Appearance.	Gas from 100 cm^3	Appearance.
	cm^3			
5 min.	0.1	No change.	Small bubble.	No change.
1 hour.	1.1	No change.		
1 day.	14	Red brown.	cm^3	
3 days.	15.3	Light brown.	9.6	Reddish purple.
4 "	15.6	" "		Turbid.
7 "	. . .	Brown, turbid.		Reddish pink.
8 "	16	Clearing by precipitation.	15.1	Clearing by precipitation.
15 "	17.3	Clear, straw-colored.	18	Nearly clear.
17 "	17.4	" " "		
35 "	17.5	" " "	18.4	Clear and colorless.

	C. H_2SO_4[1 : 1] = 12.5 per cent.		D. H_2SO_4[1 : 1] = 6.25 per cent.	
1 hour.	Small bubble.	No change.	Small bubble.	No change.
1 day.	Bubble.	" "	Bubble.	" "
3 days.	Bubble larger.	" "	Bubble larger.	" "
14 "	7.1 cm^3	Color lighter.	1 cm^3	" "
37 "	11 "	" "	3 "	" "
44 "	12 "	" "	5 "	Little change.

* Loc. cit.

The full amount of permanganate present in 100 cm^3 of each mixture should, if reduced to the lowest condition of oxidation, be capable of liberating about 28.6 cm^3 of oxygen, and every cubic centimeter of gas collected corresponds to 3.5 per cent of the entire quantity of available oxygen. In comparing the amount of gas liberated at once by 50 per cent sulphuric acid [1 : 1] (Table III, A) with the amount of reduction of the permanganate indicated under similar conditions (Table I, A) it appears that less than one-fifth (0.35 per cent) of the available oxygen of the permanganate which disappears in the action escapes solution and appears in free form. When, however, the comparison is made between the amount of gas liberated after four or five days (about 55 per cent of the total available oxygen) and the amount of reduction of the permanganate during a similar interval (Table I, C) the agreement is fairly close — within one or two per cent — the proportion of oxygen which goes to saturate the liquid being small relatively to the large absolute amount. It would seem to be evident that during this interval the breaking up of the permanganate resulted chiefly in its reduction to the lowest form of oxidation. After the seventh day in Exp. A, when a precipitate began to appear, comparatively little oxygen was set free; and on the thirty-fifth day, when the precipitation had ceased and the remaining liquid was straw-colored the amount of gas collected corresponded to about 61 per cent of the available oxygen of the permanganate. The remaining 39 per cent must have gone with the precipitated oxide or have remained in solution as a higher sulphate. That but little of the higher sulphate did remain, however, is shown by comparison of A with B, in which after thirty-five days the liquid was entirely bleached. The gas finally set free in B mounted to 64.4 per cent of the available oxygen of the permanganate, and the remainder, 35.6 per cent, would be enough to throw down about 90 per cent of the entire amount of manganese in the permanganate in the degree of oxidation of MnO_2. It is noteworthy that the stronger acid, 50 per cent [1 : 1], still

held some of the higher oxide in solution until the end, and that the acid of 25 per cent [1 : 1] allowed the decomposition to pass to completion in thirty-five days, while the smaller amounts of acid, 12.5 per cent [1 : 1] and 6.25 per cent [1 : 1], brought about in forty-four days' decomposition amounting to 42 per cent and 17.5 per cent respectively.

TABLE IV.

Percentage of H_2SO_4 [1 : 1].	Time elapsed.					Percentage of $K_2Mn_2O_8$ decomposed.
	1 day.	2 days.	3 days.	4 days.	5 days.	
10	Color unchanged.	Color unchanged.	Color unchanged.	Color unchanged. Slight sediment.	Color unchanged. Slight sediment. Slight scum.	103.6
20	Color unchanged.	Color unchanged.	Color unchanged.	Color unchanged. Slight sediment.	Color unchanged. Slight sediment.	107.4
30	Color unchanged.	Color unchanged.	Color unchanged.	Reddish tinge. Slight sediment.	Reddish tinge.	106.9
40	Color unchanged.	Color unchanged.	Tinged with reddish brown.	Reddish brown.	Reddish brown.	139.2
50	Color unchanged.	Color unchanged.	Reddish brown.	Reddish brown.	Red brown.	157.4
60	Color redder.	Color redder.	Reddish brown.	Sherry brown.	Reddish olive.	158.9
70	Color redder.	Color redder.	Sherry brown.	Reddish olive.	Reddish olive.	161.1

It seemed to be desirable in this connection to make the experiments detailed in Table IV, in which note is made of changes in color and formation of precipitates in 100 cm^3 portions of liquid containing 10 cm^3 of decinormal permanganate and varying proportions of acid, during five days' standing, the degree of decomposition of the permanganate being finally determined, as in the experiments of Tables I

question of the action of potassium permanganate during oxidations carried on in the presence of sulphuric acid is obvious; for, if the aqueous acid is able to liberate permanganic acid in such proportions as to be spontaneously unstable, it is reasonable to presume that any reducing substance present at the time of such action may, by virtue of its attractive action upon the oxygen of many more molecules of the permanganic acid than would be necessary to supply the exact amount needed for perfect oxidation, tend to increase the general instability of the already unstable molecules and so set up a far-reaching decomposition. It seems to us that these considerations throw some light upon the phenomena observed by Brauner* in the oxidation of tellurous oxide in presence of sulphuric acid; and the fact that the liberation of free oxygen in this special case is more noticeable than in the oxidation of ferrous salts or oxalic acid, for example, is explicable in the light of Brauner's observation that the attraction of tellurous oxide for oxygen is greatly inferior to that of these substances — not sufficient, in fact, to break up so unstable a substance as manganic sulphate, which is at once reduced by ferrous salts or oxalic acid. The practical lesson to be drawn is the desirability of keeping the acid present in oxidations effected by the agency of permanganate at the lowest limit consistent with perfect oxidation.

In Table V are recorded the results of a comparison made between Brauner's two excellent methods for the determination of tellurous oxide by titration with potassium permanganate — the one in alkaline solution, the other in acid solution — in which the precaution suggested as to the restriction of the amount of acid which should be present was taken. The tellurous oxide used in these experiments was prepared from the so-called pure crystallized element by oxidation with nitric acid and the prepared and ignited oxide was dissolved in potassium hydroxide.

In series A the alkaline solution of the oxide was diluted

* Loc. cit.

to 100 cm^3, potassium permanganate was added in excess, sulphuric acid [1 : 1] was introduced to an amount not exceeding by more than 5 cm^3 that needed for neutralization, oxalic acid was added in excess of the amount needed to destroy the manganic oxide and permanganate, the liquid was warmed to about 80° C., and the surplus of oxalic acid was titrated by permanganate.

TABLE V.

A.				
	TeO_2 taken.	TeO_2 found.	Error.	Mean Error.
	grm.	grm.	grm.	grm.
(1)	0.1200	0.1199	0.0001−	
(2)	0.0783	0.0783	0.0000	
(3)	0.0931	0.0938	0.0007+	
(4)	0.1100	0.1116	0.0016+	0.0006+
(5)	0.0904	0.0907	0.0003+	
(6)	0.1065	0.1077	0.0012+	
B.				
	TeO_2 taken.	TeO_2 found.	Error.	Mean Error.
	grm.	grm.	grm.	grm.
(1)	0.0910	0.0912	0.0002+	
(2)	0.0910	0.0908	0.0002−	
(3)	0.0911	0.0922	0.0011+	
(4)	0.0913	0.0913	0.0000	0.0003+
(5)	0.0912	0.0913	0.0001+	
(6)	0.0914	0.0921	0.0007+	

In series B the alkaline solution of the oxide was treated with sulphuric acid [1 : 1] until the precipitate first thrown down was just redissolved, and 1 cm^3 of the same acid was added in excess. Permanganate was added in excess and oxalic acid in excess of the permanganate, the liquid was warmed, and titration by permanganate to the final reaction was completed as usual. In the calculation of the results the atomic weight of tellurium used by Brauner in his work* was adopted and the figures obtained correspond fairly well

* Loc. cit., p. 240.

(without the application of any correction) with theory based upon this assumption. Our purpose, however, was simply to test the agreement between titrations made in alkaline solution and those carried out in acid solution.

The agreement between the indications of the two methods is evidently close, and it is suggestive that that error which is slightly the larger, and also in the direction indicative of larger expenditure of the permanganate in producing the effect sought, is found on the side of the determinations made in alkaline solution.

As to the correlative question of the liberation of oxygen during oxidations by potassium permanganate in alkaline solution we have made no experiments, but experience (not detailed in this paper) in the collection of the gas liberated in oxidations effected in presence of acid leads us to distrust the evidence of such experiments unless the amount of gas liberated is considerable. While, on the one hand, small quantities of liberated gas may be so completely absorbed as not to appear free at all, it often transpires, on the other hand, that the simple admixture of unlike liquids — such, for example, as a solution of potassium permanganate with sulphuric of strength insufficient to liberate oxygen — may bring about a very appreciable liberation of dissolved gases. So far as appears, however, the proof of the liberation of oxygen in oxidations by potassium permanganate in alkaline solutions now rests upon evidence of that nature only.

XX

THE QUANTITATIVE DETERMINATION OF RUBIDIUM BY THE SPECTROSCOPE.

By F. A. GOOCH and J. I. PHINNEY.*

In a recent paper issued from this laboratory† the possibility of determining small amounts of potassium quantitatively by means of the flame spectrum was demonstrated. The work which we are about to describe was performed in the endeavor to see how far similar methods might be applicable to the quantitative determination of rubidium. It was shown in the former work that hollow coils of platinum wire may be adjusted to hold definite amounts of liquid, and that, by taking care to plunge the coil while hot into the liquid and to remove it from the liquid with its axis inclined obliquely to the surface, it is possible to take up constant amounts through a long series of experiments. It thus becomes possible to bring definite amounts of any soluble substance into a flame to be viewed spectroscopically. The potassium salt best adapted to spectroscopic use proved to be the chloride, and it was found to be advantageous to dry the coils over a hot radiator before introducing them into the flame. A large Muencke burner gave the best sort of flame; an ordinary single prism spectroscope provided with an adjustable slit (the width of which we were able to fix by closing it upon wires of known diameter) and an observing telescope movable so that different portions of the spectrum might be shut out at will, served sufficiently well for the work. The coils were made of No. 28 platinum wire (0.32 mm. in diameter) wound in about thirty turns to a

* From Am. Jour. Sci., xliv, 392.

† Gooch and Hart: Am. Jour. Sci., xlii, 448. This volume, p. 92.

spiral 1 cm. long by 2 mm. in diameter and twisted together at the ends to form a long handle. With the apparatus described it was found possible, under the most favorable conditions, to recognize the characteristic red line of the potassium spectrum when only $\frac{1}{1000}$ mg. of potassium, in the form of the chloride, was brought to the flame. It appeared, furthermore, that a comparison of the brightness of two spectra produced in close succession could be made with all the accuracy to be anticipated in photometric measurements, and that therefore by gradual dilutions and successive testings a solution of potassium chloride of unknown strength could be brought to the point of containing as much potassium to the coil-full (and so, of course, to the cubic centimeter or any other chosen volume) as a standard solution of known strength. By noting the final volume to which such an unknown solution was brought in the process of equalizing its spectrum with that of the standard, its total contents in potassium was determined. In this manner the strength of solutions of pure potassium chloride proved determinable with accuracy, but when the effect of intermixing pure sodium chloride with the potassium salt was studied it transpired that the brilliance of the potassium spectrum was markedly increased by the presence of the sodium in the flame, the maximum increase, which amounted to twenty per cent, appearing when the ratio of sodium chloride to potassium reached 100 : 1. It was found, however, that the practical difficulty of determining potassium in presence of sodium could be largely overcome by taking the precaution to bring the test solution and the standard to apparent equality as regards the potassium line, then to bring the solutions to an equality in respect to the sodium line by addition of sodium chloride to the standard, and finally to readjust the volumes of test and standard until the potassium lines were again equal. The accuracy of the determination of the potassium is, however, in spite of the precaution, somewhat affected by the presence of sodium, — the error, though, sometimes falling as low as $\frac{1}{10}$ mg. in 10 mg., rising

occasionally to 1 mg. in 15 mg. With the excellent gravimetric method which we possess for the determination of potassium, recourse would, naturally, never be taken to the spectroscopic method except in cases where small absolute amounts are concerned, but in such cases the spectroscopic method may prove a convenience.

In the work upon potassium the observations of the red line were made in the ordinary laboratory in diffused light, but preliminary experimentation upon the rubidium spectrum immediately developed the fact that the blue lines are better to work by in the case of this element, and that a dark room becomes a necessity. For the experiments to be described pure rubidium chloride was prepared by many fractional precipitations by alcohol out of aqueous solutions, and in settling the question as to the coils which should be used the choice fell upon the size holding 0.02 grm. of water and made of the No. 28 wire, the superior stiffness of these and consequent constancy in capacity giving them the advantage over smaller coils of finer wire, though the latter are capable of bringing out greater sensitiveness of the reaction. We found, for example, that under the most favorable conditions as to height of flame and width of slit, 0.0002 mg. of rubidium chloride produced the blue lines at the last limit of visibility when the larger and heavier coil was in the flame; with a coil holding 0.006 grm. of water and made of very fine wire, the more immediate volatilization of the chloride so increased the delicacy of the spectroscopic reaction that it was possible to see the lines from 0.00005 mg. of the salt. These figures serve as an indication of the possible delicacy of this method of producing spectra, but it should be remembered that all eyes do not see the rubidium lines with equal ease.

In experimenting with rubidium sulphate in place of the chloride the lighter coil appeared to lose its advantage in point of delicacy of the indication over the larger coil, possibly because the amount of metal introduced into the flame has less influence upon the rate of vaporization of the less

volatile sulphate, and the lines of the sulphate appeared equally distinct and of longer duration than those of the chloride; but while we judged the sulphate to be rather preferable in qualitative work, our earlier preliminary quantitative experiments led us to abandon it for the purposes of our investigation on account of the great uniformity in the lines yielded by the chloride. We found it desirable in comparative tests of brightness to employ as the standard the lines given by amounts of the chloride not exceeding 0.0005 mg. to 0.0007 mg., to set the slit at a width of 0.2 mm., and to bring the coils to the flame in sets of three — the first, usually a standard, serving to fix the position of the lines so that the comparative distinctness of the lines given by the other two might be the more readily determined. The tables below contain the record of an attempt to dilute a solution of the pure chloride to the strength of the standard solution under the guidance of comparative tests of the brilliance of the spectral lines yielded by the residue left upon the wires after the evaporation of the solutions taken up by coils of equivalent capacity. Dilu-

EXPERIMENT I.

Standard. Rubidium in a coil-full ($\frac{1}{50}$ cm³).	Test (known to contain 10 mg. Rb.). Volume in cm³.	Line of test compared with standard.
mg.	cm³	
0.0005	200	Brighter.
0.0005	300	Brighter.
0.0005	350	Brighter.
0.0005	370	Brighter.
0.0005	390	Brighter.
0.0005	400	Brighter (faintly).
	400	Brighter (faintly).
	400	Doubtful.
0.0005	410	Brighter (faintly).
	410	Weaker.
0.0005	420	Equally bright.
	420	Weaker.
0.0005	430	Invisible.

Found $410 \times 50 \times 0.0005 = 10.25$ mg.
Taken . . . . . $= 10$ "
Error . . . . . $= 0.25$ " $= 2.5$ per cent.

estimated amount of rubidium in the test-solution given by multiplying the volume in cubic centimeters by the number of coil-fulls in 1 cm^3 and the product by the amount of rubidium contained in a coil-full of the standard solution.

These results make it plain that when the comparison is made between solutions of pure rubidium chloride the spectroscopic method is capable of yielding fair approximations to truth. In the practical determination of rubidium, however, the question of the effect of the presence of sodium and potassium which naturally accompany it is of importance. Attention was therefore turned next to the consideration of this point, and the record of observations as to the influence of sodium upon the brightness of the rubidium spectrum is contained in the accompanying tabular statement.

Standard. Rubidium in a coil-full ($\frac{1}{10}$ cm^3).	Test-solution. Sodium in a coil-full.	Comparison of lines of test by pairs.	Comparison of lines of test with standard.
mg.	mg.		
0.00066	0.00026 0.00260	Slightly brighter. Slightly fainter.	Brighter.
0.00066	0.00130 0.00260	Equally bright.	Brighter.
0.00066	0.00260 0.00520	Equally bright.	Brighter.
0.00066	0.00260 0.00660	Brighter. Fainter.	Brighter.
0.00066	0.00260 0.00780	Brighter. Fainter.	Brighter.
0.00066	0.00260 0.01500	Brighter. Invisible on account of glare.	Brighter. Invisible.

It appears that within limits the presence of sodium in the flame increases the brilliance of the rubidium spectrum. The brightness of the lines is raised under the conditions to a maximum by the presence of sodium to forty per cent of the weight of the rubidium, and increase in the amount of sodium does not further influence the brightness of the lines until the proportion of sodium to rubidium is as ten to one; or, speaking broadly, the difference between the dissociating

action of sodium upon the rubidium chloride (to which we attribute the effect noted) does not appear to be materially different whether one or a score of molecules of sodium chloride are present to one of the rubidium chloride. But when the proportion of sodium to rubidium much exceeds ten to one the glare of light diffused through the entire spectrum (though the sodium line itself may be cut off) begins to affect the vision, and as the increase advances ultimately extinguishes the rubidium lines utterly. The degree of increase in brilliance when the lines are at a maximum was determined by diluting the test-solution until a coil-full gave a line equally brilliant with that of the standard.

Standard. Rubidium in a coil-full ($\frac{1}{75}$ cm³).	Test-solution. Rubidium in a coil-full with $\frac{1}{75}$ of its weight of sodium.	Line of test compared with standard.
mg.	mg.	
0.00066	0.00066	Brighter.
0.00066	0.00048	Brighter.
0.00066	0.00046	Brighter.
0.00066	0.00044	Equally bright.

It is plain that at the maximum degree of brilliance the sodium is responsible for an increase of fifty per cent in the brightness of the lines.

The details of similar experiments in which potassium chloride was introduced into the flame with the pure rubidium chloride are given in the following tabular statement.

From these results it appears that the presence of potassium produces an effect upon the rubidium lines similar to that of sodium; and, furthermore, the addition of 0.0004 mg. of potassium in the form of chloride to 0.00066 mg. of rubidium also in the form of chloride brings out the maximum brightness which is not materially changed by further addition of potassium up to about 0.0013 mg., but that the increase of the potassium to 0.0034 mg. results in diminution of brightness. In other words, it seems that a single molecule of potassium chloride has approximately the same dissociating effect upon the molecule of rubidium chloride in

Standard. Rubidium in a coil-full ($\frac{1}{10}$ cm³).	Test-solution. Potassium in a coil-full.	Comparison of lines of test taken by pairs.	Comparison of lines of test with standard.
mg.	mg.		
0.00066	0.00020	Slightly fainter.	Brighter.
	0.00040	Slightly brighter.	
0.00066	0.00020	Fainter.	Brighter.
	0.00340	Brighter.	
0.00066	0.00040	Equally bright.	Brighter.
	0.00066		
0.00066	0.00040	Brighter.	Brighter.
	0.00340	Fainter.	
0.00066	0.00066	Equally bright.	Brighter.
	0.00132		
0.00066	0.00066	Brighter.	Brighter.
	0.00346	Fainter.	
0.00066	0.00066	Brighter.	Brighter.
	0.00660	Fainter.	
0.00066	0.00066	Brighter.	Brighter.
	0.01320	Fainter.	
0.00066	0.00066	Brighter.	Brighter.
	0.02000	Fainter.	Equally bright.
0.00066	0.00066	Brighter.	Brighter.
	0.02660	Fainter.	Equally bright.
0.00066	0.00066	Brighter.	Brighter.
	0.03340	Fainter.	Equally bright.
0.00066	0 00066	Brighter.	Brighter.
	0.03340	Invisible.	Invisible.

the flame as that brought about by a greater number, that the presence of potassium in the proportion of five parts to one of the rubidium begins to influence visibility unfavorably, that when this proportion rises to thirty to one of the elements (or twenty to one of the chlorides) the lines appear about as distinctly as if no potassium were present, and that an increase of proportion to fifty to one may bring about a sufficient glare of light to reduce the rubidium lines to invisibility. The degree of increase in brilliance due to the action of potassium when that element is present in proportions suitable to induce the maximum effect is shown in the following record.

It appears that the presence of 0.00044 mg. of potassium is capable of increasing the brilliance of the lines yielded by 0.00044 mg. of rubidium to an equality with the lines given by 0.00066 mg. of the pure salt; or, that the maximum increase of brightness amounts to fifty per cent.

Standard. Rubidium in a coil-full ($\frac{1}{10}$ cm³.)	Test-solution. Rubidium in a coil-full with its own weight of potassium.	Line of test compared with standard.
mg.	mg.	
0.00066	0.00066	Brighter.
0.00066	0.00064	Brighter.
0.00066	0.00057	Brighter.
0.00066	0.00049	Brighter.
0.00066	0.00044	Equally bright.
0.00066	0.00040	Faint.

It is evident, therefore, that means must be found to effect the separation of the rubidium from sodium and potassium, or of bringing test and standard to the same condition as regards the presence of these elements, before any reasonable degree of accuracy can be expected in the spectroscopic determination of rubidium as it ordinarily occurs in nature. The separation from sodium is easily accomplished by the conversion of the salts to the form of chloroplatinates; but for the quantitative separation of rubidium from potassium there is no good method known. The question as to the practical value of the spectroscopic reaction of rubidium for purposes of approximative quantitative analysis resolves itself into the problem as to whether by matching potassium lines as well as the rubidium lines (following the method outlined in the determination of potassium in presence of sodium), and so bringing the lines of test and standard equally under the influence of potassium, it is possible to make the comparison between the rubidium lines trustworthy. It was shown in the former paper that in matching solutions of potassium by means of the red line there is no difficulty; but the convenience of being able to use the spectroscope without readjustment throughout the entire experiment made it desirable to see whether the blue line of potassium might not serve sufficiently well in the comparison. It is hardly necessary to reproduce here in detail the evidence bearing upon this point, but we found as the result that the potassium may be determined by the use of the blue line with an error amounting to 10 per cent or 20 per cent, which, though far

greater than that inherent in the use of the red line, admits of the attainment of determinations which should be accurate enough for the present purpose. We proceeded, therefore, to make a determination of rubidium in presence of potassium by the process referred to, the details of which are given in Experiment IV.

It is evident that the percentage error is considerable, but inasmuch as the application of the process would naturally be to the determination of small absolute amounts of rubidium we thought it desirable to go a step further to see whether means are at hand for separating large amounts of potassium from small amounts of rubidium with an approach

EXPERIMENT IV.

Standard solution containing { 0.0005 mg. rubidium / 0.0015 " potassium } to the coil-full.
Test solution contained 8 mg. rubidium and no potassium.

Step 1.	Step 2.	Step 3.	Step 4.	Step 5.
Preliminary test for Rb.	Preliminary matching of K line.	Rematching of Rb line.	Readjustment of K line.	Final matching of Rb line.
Test at 20 cm^3 gave Rb line like standard.	Test at 20 cm^3 gave K line like standard when 1 mg. of K had been added.	Test at 35 cm^3 gave Rb lines like standard.	Test at 35 cm^3 gave K line like standard when 2 mg. were present.	Test at 35 cm^3 gave Rb line like standard.

Rubidium found $35 \times 50 \times 0.0005 = 0.875$ mg.
" taken . . . . . $= 0.8$ "
Error . . . . . $= 0.075$ " $= 9.4$ per cent.

sufficiently near to completeness to bring the potassium present within the limits allowed by the spectroscopic method. After some experimentation we fixed upon the simplest possible procedure, viz.: the solution of the salts in the least possible amount of water, precipitation of the mass of potassium chloride by addition of alcohol, filtration, and the evaporation of the filtrate. In Experiments V, VI, VII, this mode of working was put to the proof. The amounts of

rubidium indicated were dissolved in the form of the chloride in water, 0.1 grm. of potassium chloride was added, and the solution was evaporated and treated as described.

	Rubidium taken in the form of chloride.	Potassium taken in the form of chloride.	Rubidium found.	Absolute error.	Error.
	mg.	grm.	mg.	mg.	per cent.
V.	1	0.1	0.8	0.2	20
VI.	2	0.1	1.7	0.3	15
VII.	1	0.1	0.9	0.1	10

The error of the process is manifestly large, and only roughly approximate results can be hoped for when large amounts of rubidium are dealt with; but if the question is the estimation of only a few milligrams of rubidium, it will appear, we think, in view of the fact that the only alternative is an indirect process, that even this great error is not absolutely prohibitive of what may be called fair determinations.

XXI

A METHOD FOR THE QUANTITATIVE SEPARATION OF BARIUM FROM STRONTIUM BY THE ACTION OF AMYL ALCOHOL ON THE BROMIDES.

By PHILIP E. BROWNING.*

THE existing methods upon which dependence can be placed in the separation of barium from strontium are few in number. R. Fresenius in discussing them through several numbers of his journal † concludes that the only one which gives perfectly reliable results consists of the precipitation of the barium by a double treatment with ammonium chromate in acetic acid solution. Having demonstrated the possibility of separating both barium and strontium from calcium by the dehydrating and appropriate solvent action of boiling amyl alcohol on the nitrates ‡ the possibility of a similar method of separation by the use of suitable salts of barium and strontium seemed worthy of investigation and necessary to complete the series as applied to this group. In looking about for suitable salts upon which to experiment, the behavior of the chlorides was suggestive. Barium chloride is completely insoluble in amyl alcohol, while the corresponding strontium salt is somewhat soluble. The possibility of finding strontium bromide more readily soluble than the corresponding chloride seemed worthy of attention. The method of preparation followed was the treatment of the precipitated and thoroughly washed carbonates of barium and strontium with hydrobromic acid prepared § by mixing definite proportions of potassium bromide

* From Am. Jour. Sci., xliv, 459.

† Zeitschr. anal. Chem., xxix, 20, 143, 413.

‡ Am. Jour. Sci., xliii, 50, 314. This volume, pp. 107, 116.

§ Proc. Amer. Acad., xvii, 30.

in solutions with sulphuric acid and water while hot, filtering off the potassium sulphate which separates on cooling, and redistilling the filtrate until the distillate contains no appreciable trace of sulphuric acid. The standards of the solutions of barium and strontium bromides made in this way were determined by precipitating definite portions, measured and weighed, with sulphuric acid, — the strontium after the accepted method of adding ethyl alcohol to increase the insolubility and the barium after the manner suggested by Mar,* precipitating with an excess of sulphuric acid in the presence of hydrochloric acid. The mean of closely agreeing results was taken as the standard. Preliminary experiments on the bromides formed in this way gave encouraging results, the barium salt appearing to be almost completely insoluble while the strontium salt dissolved freely. The first series of experiments were directed toward a quantitative determination of the solubility of barium bromide in the alcohol. Definite portions of the standardized solution of barium bromide were measured from a burette into counterpoised beakers of about 50 cm^3 capacity and weighed as a check on the burette reading. This solution was then evaporated to dryness, and the residue was dissolved in a few drops of water and boiled with 10 cm^3 of amyl alcohol. The separating bromide was filtered off on an asbestos felt contained in a perforated platinum crucible, the whole having been previously ignited and weighed. The crucible containing the bromide was at first dried at 140°–150° C. in an air bath after the manner described in the previous papers, and weighed. The unsuccessful attempt to get a constant weight, however, proved the impossibility of weighing as bromide, the weight decreasing rapidly with each successive drying. It was deemed best, accordingly, to dissolve the bromide from the felt into a beaker placed to receive it, and to precipitate with sulphuric acid in the presence of hydrochloric acid, after the same manner followed in the determinations of the standards. The precipitated sulphate, which in a few minutes settles completely, was

* Am. Jour. Sci., xli, 288. This volume, p. 63.

filtered off upon the same felt from which the bromide had been dissolved, dried, ignited to low redness, and weighed. Series I gives the results of several experiments made after this manner which show the solubility of the barium salt to be about 0.0013 grm. on the oxide in 10 cm^3 of amyl alcohol. The filtrate after boiling with amyl alcohol was evaporated and the residue was treated with sulphuric acid and weighed; or the filtrate was precipitated directly by dilute sulphuric acid, enough ethyl alcohol being added to secure thorough mixture. The amount of sulphate found agreed uniformly with the loss determined in the residue after boiling. A portion of the salt which dissolved in the alcohol on being examined before the spectroscope gave only the green bands characteristic of barium.

SERIES I.

	BaO taken.	BaO found.	Error.
	grm.	grm.	grm.
(1)	0.1234	0.1222	0.0012–
(2)	0.0824	0.0809	0.0015–
(3)	0.0823	0.0809	0.0014–
(4)	0.0818	0.0803	0.0015–
(5)	0.0733	0.0720	0.0013–

Several methods of treatment were followed to prevent if possible this solubility, such as the addition of a few drops of hydrobromic acid before boiling, of the same after the barium bromide had separated, of a few drops of ethylene dibromide or ethyl bromide at the completion of the boiling, of a few drops of bromine water before boiling, etc. The results of these experiments showed these modifications to be of little or no value.

On boiling the strontium bromide with the alcohol slight spots separated occasionally, which on the addition of a drop of hydrobromic acid went into solution and did not appear on re-boiling. In order to determine the solubility of the strontium bromide in the alcohol a saturated solution was obtained by boiling an excess of the strontium salt with the alcohol, the

salt in a measured portion of 10 cm^3 was precipitated as sulphate by the addition of ethyl alcohol and sulphuric acid, and weighed. Duplicate determination showed the solubility to be about 0.2 gram on the oxide in 10 cm^3 of the alcohol. The mode of procedure for the separation of these elements was identical with that already described in the case of barium alone up to the point at which the barium was filtered off, except, of course, the addition at first of a measured and weighed amount of a previously standardized solution of strontium bromide. The strontium was precipitated from the filtrate as sulphate by dilute sulphuric acid, ethyl alcohol being added to secure thorough mixture. These precipitates were generally filtered off upon asbestos felts, although their gelatinous character delayed the filtration somewhat, and thus the drying and burning of a filter paper with the possible danger of loss by reduction in the presence of burning paper was avoided. Series II gives the results of a single treatment, and it will be seen that there is apparently a slight contamination of the barium by the strontium which where the latter is present in large quantities balances the solubility of the barium (0.0013 grm. on the oxide). Where the amounts of strontium taken are small the loss of barium due to solubility appears.

SERIES II.

	BaO taken.	BaO found.	Error.	SrO taken.	SrO found.	Error.
	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.1228	0.1225	0.0003—	0.1070	0.1065	0.0005—
(2)	0.1227	0.1231	0.0004+	0.1074	0.1069	0.0005—
(3)	0.1224	0.1228	0.0004+	0.1070	0.1067	0.0003—
(4)	0.1217	0.1201	0.0016—	0.0364	0.0372	0.0008+
(5)	0.1216	0.1222	0.0006+	0.0133	0.1124	0.0009—
(6)	0.0974	0.0970	0.0004—	0.0719	0.0721	0.0002+
(7)	0.0971	0.0973	0.0002+	0.0730	0.0727	0.0003—
(8)	0.0970	0.0971	0.0001+	0.0718	0.0716	0.0002—
(9)	0.0411	0.0390	0.0021—	0.0365	0.0385	0.0020+
(10)	0.0243	0.0234	0.0009—	0.1072	0.1072	0.0000

Series III gives the result of a double treatment. In this series the contaminating effect of the strontium salt disappears almost entirely, leaving a deficiency of about 0.0025 grm. on

the oxide to be added to the barium, and a corresponding amount of sulphate (0.0040 grm.) to be subtracted from the strontium sulphate before calculating it to the condition of the oxide. The manipulation is the same as that outlined for the single treatment, as far as the completion of the first boiling. At this point the amyl alcohol containing most of the strontium in solution was decanted upon a weighed and ignited felt and collected in a beaker placed to receive it. The residue of barium with traces of strontium was then dissolved in a few drops of water, a drop of hydrobromic acid was added, and the boiling was repeated with another portion of 10 cm^3 of amyl alcohol. Upon reaching the boiling point of the alcohol the beaker was removed, and the barium salt was filtered upon the felt through which the first portion had been decanted, and treated as before described.

SERIES III.

	BaO taken.	BaO found (corrected).	Error.	SrO taken.	SrO found (corrected).	Error.
	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.1212	0.1219	0.0007+	0.1068	0.1071	0.0003+
(2)	0.1215	0.1219	0.0004+	0.0358	0.0359	0.0001+
(3)	0.1220	0.1221	0.0001+	0.0353	0.0347	0.0006—
(4)	0.1212	0.1220	0.0008+	0.0363	0.0358	0.0005—
(5)	0.1219	0.1221	0.0002+	0.0361	0.0354	0.0007—
(6)	0.1211	0.1218	0.0007+	0.1126	0.1116	0.0010—
(7)	0.1319	0.1319	0.0000	0.0577	0.0586	0.0009+
(8)	0.0496	0.0492	0.0004—	0.0574	0.0579	0.0005+

The method is rapid, and while the correction to be applied owing to the solubility of the barium salt is large, it is so definite that it cannot be objectionable.

XXII

ON THE DETERMINATION OF IODINE IN HALOID SALTS BY THE ACTION OF ARSENIC ACID.

By F. A. GOOCH and P. E. BROWNING.*

Three years ago we demonstrated † the possibility of determining iodine in mixtures of alkaline chlorides, bromides, and iodides, with rapidity and exactness, by taking advantage of the behavior of arsenic acid toward the haloid salts in presence of sulphuric acid of definite strength. We showed in brief, that when amounts of potassium iodide ranging from 0.005 grm. to 0.5 grm. were dissolved in 100 cm^3 of water containing 2 grm. dihydrogen potassium arseniate and 20 cm^3 of a mixture of sulphuric acid with water in equal volumes, the entire amount of iodine was expelled on boiling down the solution from 100 cm^3 to 35 cm^3; and further, that arsenic, reduced to the arsenious condition to an amount the exact equivalent of the iodine liberated, remained in solution and was determinable, after neutralization of the acid, in presence of an alkaline bicarbonate, by titration against standard iodine according to Mohr's classical method. We studied carefully the behavior of alkaline bromides and chlorides under identical conditions, and determined that 0.5 grm. of potassium bromide acted upon the mixture of arseniate and acid to the extent of reducing arsenic equivalent to 0.0008 grm. of iodine, and that 0.5 grm. of sodium chloride did not reduce arsenic but did cause, under the conditions, a volatilization proportional to the amount of arsenious oxide present, the loss amounting at the most — when 0.56 grm. of the iodide was present to exert its reducing action upon the arsenic — to 0.0011 grm. We

* From Am. Jour. Sci., xlv, 334.

† Am. Jour. Sci., xxxix, 188. This volume, p. 1.

showed, furthermore, that these maximum errors, due to the action of bromides and chlorides, though not large and tending to neutralize one another when both bromides and chlorides are present, may be eliminated by the application of a numerical correction to the results whenever the amounts of bromide and chloride present become known.

Recently Friedheim and Meyer * have recognized the value of our reaction and applied it to the elimination of iodine from mixtures of haloid salts. They have, however, taken issue with us (unadvisedly, as we think) as to matters of detail. They have, in the first place, put themselves upon record as being unable to titrate arsenious oxide by iodine in alkaline solution under the conditions of our process. They account for their failure by the wholly unsupported hypothesis that the iodine reaction is unavailable in presence of the amounts of salts present, and modify the treatment by distilling, collecting the iodine in the distillate, and determining it by the thiosulphate method, thus introducing complexity of apparatus and manipulation, and sacrificing the simplicity and rapidity which are chief advantages of our process. Had they read our paper with intelligent care it must have been evident that we had given special attention to the question of the influence of the salts present upon the iodine reaction; for we expressly stated that "due correction was made for the amount of iodine necessary to develop the test-color in a solution prepared and treated similarly in all respects to the experimental solutions excepting the introduction of the iodide — the correction amounting to a single drop more of the decinormal iodine than was required to produce the end reaction in the same volume of pure water containing only the starch indicator." It is obvious that such errors as 0.003 to 0.006 grm., which Friedheim and Meyer found even in the absence of bromides and chlorides, are not explicable by the action of the salts which we used. Our errors ranged under like conditions from 0.0009 grm. — to 0.0003 grm. +, with a mean error in nine determinations of 0.0002 grm. —.

* Zeitschr. anorg. Chem., i, p. 407.

Everybody knows that the starch iodide test is most delicate in acid solutions and in presence of combined iodine, but Mohr's method of titrating arsenious oxide and iodine against one another in alkaline solution is sufficiently delicate for very exact work, provided only that the alkali in excess is in the form of the bicarbonate, that the starch emulsion is used in abundance, and that the volumes of solutions titrated are regulated to low and uniform measure. In many determinations of iodine made by our method at different times and with different materials it has never been our ill-fortune to chance upon results so extraordinary as those of Friedheim and Meyer, though we have met in the course of our work with potassium arseniate so contaminated with nitrates as to be unfit for use and with alkaline hydroxides too impure to employ. Most analytical processes depend for their exactness upon the use of proper materials; ours is no exception to the rule in this regard.

As to the correctness of the main reaction there appears to be no difference of opinion between Friedheim and Meyer and ourselves. We have, therefore, taken the pains, perhaps unnecessarily, to make experiments in which the estimation of the iodine of the same identical portions is effected both in the distillate and in the residue, in order that the two modes of estimation may be brought into direct comparison. It is scarcely needful to add that we took care to work with pure reagents. The potassium iodide, like that which we employed in our former investigation, was prepared by acting with resublimed iodine upon an excess of iron wire, pouring off the solution from the iron when the color of iodine had vanished, adding iodine equal to one-third the amount of that originally used, pouring the filtered liquid into a boiling solution of the calculated equivalent of potassium carbonate (from the bicarbonate), and filtering off the precipitated magnetic oxide of iron. The slightly alkali solution thus made, containing approximately 2 grm. of pot um iodide in 100 cm^3, and free from chlorine d mine, s standardized by precipitating the iodi as in the form of silver iodide

and weighing upon asbestos. The other reagents — the sulphuric acid, the sodium hydroxide, the acid potassium carbonate, the dihydrogen potassium arseniate — when present in the proportions used in our process, and mixed with 5 cm^3 of clear starch solution prepared by Gastine's* formula (5 grm. starch, 0.01 HgI_2, 1 litre of water) gave the starch blue with a single drop of decinormal iodine at all dilutions below 300 cm^3. The results of these experiments are given in the following table.

	Iodine taken in form of KI.	Iodine found in residue by our method.	Iodine found in distillate by As_2O_3.	Iodine found in distillate by $Na_2S_2O_3$.	Error in residue.	Error in distillate.
	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.4054	0.4052	. . .	. . .	0.0002−	. . .
(2)	0.4057	0.4055	. . .	. . .	0.0002−	. . .
(3)	0.4054	0.4052	. . .	. . .	0.0002−	. . .
(4)	0.4054	0.4052	. . .	. . .	0.0002−	. . .
(5)	0.4042	0.4046	0.4046	. . .	0.0004+	0.0004+
(6)	0.4050	0.4052	0.4040	. . .	0.0002+	0.0010−
(7)	0.4050	0.4052	. . .	0.4039	0.0002+	0.0011−
(8)	5.4058	0.4052	. . .	0.4051	0.0006−	0.0007−
(9)	0.4054	0.4046	. . .	0.4051	0.0008−	0.0003−
(10)	0.4042	0.4046	. . .	0.4039	0.0004+	0.0003−
(11)	0.4055	0.4052	. . .	0.4057	0.0003−	0.0002+

Experiments (1) to (4) were made exactly in accordance with the directions of our former paper, the mixtures being simply boiled in an Erlenmeyer flask, trapped to prevent mechanical loss by hanging in the neck of the flask, with the larger end downward, a straight, two-bulbed drying tube cut off so as to leave the larger tube about 4 cm. in length.† These four experiments all gave the same result, which differed from the theory by 0.0002 grm. −. The mixtures of the remaining experiments were treated in a flask connected with a cooled receiver and absorption tubes for condensing the distilled iodine (all joints being of glass and carefully ground), and carbon dioxide was passed through the apparatus in slow current to facilitate the transfer of iodine and quiet boiling.

* Bull. Soc. Chim., l. 172.

† See Fig. 1, p. 12.

In experiments (5) and (6) the iodine was received in an alkaline solution of standard arsenious oxide, and titration was effected with standard iodine after addition of starch. The residue was treated by our method. It will be observed that the residues, which contain the large amounts of salts, yield results by titration practically identical with those obtained by treating the distillates which do not contain the large masses of salts. In experiments (7) to (11) the iodine distilled was received in potassium iodide and estimated by standard sodium thiosulphate, itself standardized against the iodine, whose value in terms of the standard arsenious oxide was also known. The residues were treated by our method. It is evident that the errors of both processes of treatment are reasonably small (respectively 0.0001 grm.– and 0.0004 grm.– in the average), with what difference there is in favor of our treatment of the residues. Our process is incomparably the more convenient and rapid. We do not doubt that Friedheim and Meyer could have obtained equally good results had they worked with pure reagents.

Friedheim and Meyer disagree with us also as to the degree of concentration of the liquid necessary to insure the complete expulsion of iodine and as to the effect of the concentration upon bromides present, — points to which we gave particular attention in our former paper. We showed that, in general, upon boiling a mixture of iodide with sulphuric acid and the arseniate diluted with water, the amount of iodine removed depended upon the proportion of the sulphuric acid to the final volume of the whole liquid, it being plainly shown that even after the liquid had lost the color of free iodine in the process of concentration it was still possible to detect combined iodine. Further concentration and, to some extent, dilution and repetition of the concentration to the former point tend to set free the residual iodine. In experimenting upon the proportions of acid most convenient for the work we found that a solution made up to contain 0.5 grm. of potassium iodide, 2 grm. of dihydrogen potassium arseniate, and 20 cm^3 of the sulphuric acid mixture (1 : 1 by volume) retained when

boiled down to 40 cm^3 no determinable free iodine and but the faintest trace of combined iodine, while at 35 cm^3 the liquid was free from iodine in any form. Upon experimenting as to the behavior of mixtures of chlorides and iodides we found that 0.5 grm. of sodium chloride added to the mixture containing 0.5 grm. of the iodide occasioned at 40 cm^3 a maximum loss of arsenious chloride equivalent to 0.0004 grm. of the oxide, or to 0.0008 grm. at 30 cm^3; and that the loss, as a matter of course, is less as the amount of iodide present (and consequently the arsenious oxide formed) is diminished. We found that 0.5 grm. of potassium bromide treated in similar manner occasioned no loss of arsenious bromide, but did induce at 35 cm^3, reduction of the arsenic acid amounting to 0.0005 grm. of iodine. Smaller amounts of bromide produced proportionately smaller effects, but concentration even a little below 35 cm^3 was likely to be productive of serious error. We fixed upon 35 cm^3, therefore, as the ideal concentration for removing iodine from unknown mixtures with chlorides and bromides, but expressly stated that failure to concentrate below 40 cm^3 introduces no appreciable error, while great care should be taken not to press the concentration below 35 cm^3 on account of the danger of bringing about the reduction of the arsenic by the bromide.

Friedheim and Meyer contend that the reduction of volume under the conditions should not be pressed beyond 50 cm^3 at the most, and cite in proof experiments in which potassium bromide in amounts less than half as great as those which we used caused an error on concentration to 35 cm^3 equivalent to five or six milligrams of iodine. They recommend boiling from 150 cm^3 to 50 cm^3 to remove the iodine without disturbing bromine. Our former experiments are sufficiently definite upon these points. We have, however, determined directly and quantitatively the amounts of iodine remaining unexpelled when solutions are boiled from 150 cm^3 to 50 cm^3, and found, in certain experiments, in which the additional iodine expelled in concentrating from 50 cm^3 to 35 cm^3 was collected in potassium iodide and estimated with sodium thiosulphate, that

about 0.0013 grm. remained when 0.5 grm. of potassium iodide was originally taken, and 0.0003 grm. when 0.25 grm. of the iodide was present at the first. It is evident, therefore, that concentration to 50 cm^3 is not sufficient when the maximum amount of iodide may be present. We have also made certain experiments — recorded below — in which the bromine liberated at different degrees of concentration was collected in potassium iodide and estimated by the iodine set free. In our former work we inferred the loss of bromine from the effects upon the arsenic acid in the residues. In these experiments solutions of potassium bromide (free from iodine), with 20 cm^3 of sulphuric acid (1 : 1), and 2 grm. of dihydrogen potassium arseniate were boiled down in a flask connected by ground glass joints with a cooled receiver containing potassium iodide and the iodine set free was estimated by standard sodium thiosulphate.

KBr taken.	Initial volume.	Final volume.	Bromine in distillate.
grm.	cm^3	cm^3	grm.
0.5	150	50	trace.
	50	40	trace.
	40	35	0.0004
0.5	50	31	0.0010
	31	26	0.0064
	26	23	0.0072
0.25	45	40	None.
	40	31	0.0004
	31	27	0.0010
0.25	50	35	0.0003
0.1	50	30	0.0003

From these results, which confirm very closely those obtained by an examination of the residues and recorded in our former paper, it is evident that the concentration may go under the most unfavorable conditions — when the maximum amount of bromide is present — to 40 cm^3 without loss and to 35 cm^3 with small loss. As we stated in our former paper, concentration below 35 cm^3 should be avoided.

In our former paper we showed that the iodine could be determined in unknown mixtures of sodium chloride, potassium

bromide, and potassium iodide taken in amounts not exceeding 1.5 grm. (in which, however, neither individual salt was present in amount exceeding 0.5 grm.) with a maximum error ranging from 0.0013 grm.— to 0.0016 grm.+. We showed, further, that when the amounts of chloride and bromide present were known also a correction for the action of these salts might be applied which would reduce the maximum errors to 0.0010 grm.— and 0.0008 grm.+, and give a mean error of 0.0001 grm.— for twenty-six determinations.

In conclusion we affirm the correctness of our former work and reiterate our former directions without change.

closely agreeing determinations was taken as the value of the standard solution. The mode of procedure in the testing was simple and may be outlined as follows: Into a counterpoised beaker a definite amount of the standardized solution of barium nitrate was drawn and the weight taken as before described, the amount of nitric acid to be used was then added, and the whole volume brought up to 90 cm^3 by the addition of water. This acid solution was then brought to the boiling point and 10 cm^3 of the dilute sulphuric acid added, and the whole was allowed to stand for the length of time shown by the table before filtering on asbestos, igniting and weighing. It will be seen that the total volume of liquid taken in each determination was uniformly 100 cm^3, the percentage of acid by volume being thus easily regulated. In no case did the amount of barium salt present exceed 0.4 gm. considered as the sulphate, and consequently the uniform amount of 10 cm^3 of dilute (1 : 4 by volume) sulphuric acid employed was always enough to assure the excess which Fresenius* has shown to be necessary in the precipitation of barium as the sulphate in the presence of hydrochloric acid. By reference to Series I it is evident that in the presence of five per cent of nitric acid very little solvent action is shown, and it appears also that the sulphate may be safely filtered after an hour's time. In the presence of ten to fifteen per cent of the acid the solvent effect is very small when the solution is allowed to stand six hours or more. With twenty to twenty-five per cent of acid present we find the solubility to be slightly increased, but even then the average loss is less than 0.001 grm.

Having shown that free nitric acid even though present in considerable amount has only a slight solvent influence upon barium sulphate, it seemed interesting to try the effect of the combination of nitric and hydrochloric acids mixed in the proportion to form aqua regia ($3HCl : 1HNO_3$). The experiments recorded in Series II show that aqua regia has even less effect as a solvent than nitric acid alone. In fact

* Zeitschr. anal. Chem., xxx, 455.

it seems to act like hydrochloric acid alone, which practically has no solvent effect, as shown by Mar's work previously cited.

SERIES I.

Exp.	$BaSO_4$ equivalent to $Ba(NO_3)_2$ taken.	$BaSO_4$ found.	Error in terms of $BaSO_4$.	Averages.	Time between precipitation and filtration.	Per cent by volume of strong HNO_3.	Total volume.
	grm.	grm.	grm.	grm.	hours.		cm^3
(1)	0.2540	0.2536	0.0004—		12	5	100
(2)	0.2489	0.2483	0.0006—	0.0006—	12	5	100
(3)	0.2495	0.2489	0.0006—		12	5	100
(4)	0.2492	0.2482	0.0010—		12	5	100
(5)	0.2486	0.2483	0.0003—	0.0002—	6	5	100
(6)	0.2490	0.2490	0.0000		6	5	100
(7)	0.2555	0.2546	0.0009—	0.0006—	1	5	100
(8)	0.2538	0.2534	0.0004—		1	5	100
(9)	0.4067	0.4057	0.0010—		12	10	100
(10)	0.2540	0.2533	0.0007—		12	10	100
(11)	0.2492	0.2489	0.0003—	0.0006—	12	10	100
(12)	0.2493	0.2488	0.0005—		12	10	100
(13)	0.2494	0.2488	0.0006—		12	10	100
(14)	0.2492	0.2492	0.0000		6	10	100
(15)	0.2490	0.2489	0.0001—	0.0002—	6	10	100
(16)	0.2489	0.2484	0 0005—		6	10	100
(17)	0.2540	0.2524	0.0016—	0.0016—	1	10	100
(18)	0.2529	0.2515	0.0014—		12	15	100
(19)	0.2534	0.2522	0.0012—		12	15	100
(20)	0.2533	0.2531	0.0002—	0.0007—	12	15	100
(21)	0.2538	0.2532	0.0006—		12	15	100
(22)	0.2497	0.2490	0.0007—		12	15	100
(23)	0.2489	0.2487	0.0002—		12	15	100
(24)	0.2542	0.2528	0.0014—		6	15	100
(25)	0.2486	0.2486	0.0000	0.0006—	6	15	100
(26)	0.2492	0.2487	0.0005—		6	15	100
(27)	0.2547	0.2532	0.0015—	0.0015—	6	15	100
(28)	0.2489	0.2478	0.0011—		12	20	100
(29)	0.2486	0.2475	0.0011—		12	20	100
(30)	0.2548	0.2546	0.0002—	0.0008—	12	20	100
(31)	0.2548	0.2542	0.0006—		12	20	100
(32)	0.2496	0.2486	0.0010—		12	20	100
(33)	0.2539	0.2527	0.0012—		6	20	100
(34)	0.2488	0.2475	0.0013—	0.0008—	6	20	100
(35)	0.2497	0.2497	0.0000		6	20	100
(36)	0.2486	0.2477	0.0009—		12	25	100
(37)	0.2491	0.2490	0.0001—		12	25	100
(38)	0.2494	0.2484	0.0010—		12	25	100
(39)	0.2538	0.2535	0.0003—	0.0008—	12	25	100
(40)	0.2492	0.2484	0.0008—		12	25	100
(41)	0.2487	0.2471	0.0016—		12	25	100
(42)	0.3414	0.3407	0.0007—		12	25	100
(43)	0.2489	0.2481	0.0008—	0.0007—	6	25	100
(44)	0.2485	0.2478	0.0007—		6	25	100

SERIES II.

	$BaSO_4$ equivalent to $Ba(NO_3)_2$ taken.	$BaSO_4$ found.	Error in terms of $BaSO_4$	Averages.	Time between precipitation and filtration.	Per cent by volume of strong aqua regia.	Total volume.
	grm.	grm.	grm.	grm.	hours.	($3HCl : 1HNO_3$).	cm^3
(1)	0.2539	0.2534	0.0005−		12	5	100
(2)	0.2540	0.2538	0.0002−	0.0002−	12	5	100
(3)	0.2490	0.2490	0.0000		12	5	100
(4)	0.2491	0.2492	0.0001+		12	5	100
(5)	0.2488	0.2484	0.0004−	0.0001−	6	5	100
(6)	0.3419	0.3421	0.0002+		6	5	100
(7)	0.2491	0.2487	0.0004−		12	10	100
(8)	0.2486	0.2482	0.0004−	0.0006−	12	10	100
(9)	0.2549	0.2539	0.0010−		12	10	100
(10)	0.2543	0.2538	0.0005−		12	10	100
(11)	0.2487	0.2485	0.0002−		6	10	100
(12)	0.3416	0.3415	0.0001−	0.0002−	6	10	100
(13)	0.3417	0.3420	0.0003+	0.0003+	1	10	100
(14)	0.2547	0.2544	0.0003−		12	15	100
(15)	0.2492	0.2492	0.0000	0.0003−	12	15	100
(16)	0.2489	0.2479	0.0010−		12	15	100
(17)	0.3412	0.3412	0.0000		12	15	100
(18)	0.3418	0.3417	0.0001−	0.0001−	6	15	100
(19)	0.3418	0.3412	0.0001−		6	15	100
(20)	0.3411	0.3402	0.0009−	0.0009−	1	15	100
(21)	0.2492	0.2484	0.0008−		12	20	100
(22)	0.2486	0.2480	0.0006−	0.0005−	12	20	100
(23)	0.2491	0.2485	0.0006−		12	20	100
(24)	0.3412	0.3411	0.0001−		12	20	100
(25)	0.3417	0.3418	0.0001+		6	20	100
(26)	0.3417	0.3417	0.0000	0.0000	6	20	100
(27)	0.3414	0.3404	0.0010−	0.0010−	1	20	100
(28)	0.2491	0.2485	0.0006−		12	25	100
(29)	0.1701	0.1697	0.0004−	0.0008−	12	25	100
(30)	0.1708	0.1705	0.0003−		12	25	100
(31)	0.1710	0.1710	0.0000		12	25	100
(32)	0.3415	0.3410	0.0005−	0.0003−	6	25	100
(33)	0.3418	0.3418	0.0000		6	25	100
(34)	0.3412	0.3405	0.0007−	0.0007−	1	25	100

In this connection I append the results of a few experiments made to determine the effect of the presence of a considerable amount of free nitric acid, on the precipitations of barium as sulphate in cases where certain substances are present which under ordinary conditions tend to hold up the precipitate. Fresenius * has demonstrated this property in

* Zeitschr. anal. Chem., ix, 62.

the case of ammonium nitrate, Scheerer and Rube* have shown that metaphosphoric acid acts similarly, and Spiller† notes the same general effect where alkaline citrates are present. Series III shows the results obtained by precipitating definite portions of the standard solution of barium nitrate in the presence of stated amounts of the substances just mentioned. The total volume in every case was 100 cm^3,

SERIES III.

Exp.	Impurity present to the amount of 5 grm.	$BaSO_4$ equivalent to $Ba(NO_3)_2$ taken.	Apparent amount of $BaSO_4$ found.	$BaSO_4$ after purification.	Error after purification.	Percentage of strong HNO_3 by volume.
		grm.	grm.	grm.	grm.	
(1)	Ammonium nitrate	0.1710	0.1800	0.1702	0.0008−	10
(2)	" "	0.3415	0.3440	0.3410	0.0005−	10
(3)	" citrate	0.3412	0.3442	0.3407	0.0005−	10
(4)	Sodium "	0.1360	0.1730	0.1366	0.0006+	10
(5)	Metaphosphoric acid	0.3461	0.3511	0.3470	0.0009+	10

the amount of dilute sulphuric acid used 10 cm^3, and the time between precipitation and filtration twelve hours. Upon filtering, igniting, and weighing the barium sulphate an excess of weight, due undoubtedly to contamination of the precipitate, was found. It became necessary, therefore, to purify the precipitate as first weighed, in order to determine whether all the barium was actually precipitated or whether a partial loss was covered by the amount of included impurity. The method of purification employed was that successfully applied by Mar in the work previously mentioned. The contaminated sulphate collected on paper and treated according to the familiar method (on account of the difficulty attending the complete removal of the precipitate from asbestos for purposes of purification), was dissolved in warm concentrated sulphuric acid, and evaporated quickly and without spattering by means of the Hempel burner, the barium sulphate being left after this treatment in coarse

* Jour. prakt. Chem., lxxv, 113–116.

† Chem. News, viii, 280–281.

granular crystals. The crystallized sulphate was warmed with a little water containing a drop of sulphuric acid, filtered upon an asbestos felt contained in a perforated platinum crucible, the crucible and felt having been previously ignited and weighed.

The results show that in the presence of nitric acid amounting to one-tenth by volume of the entire liquid these salts exert no apparent interference with the precipitation of the barium.

The entire work would seem to show that the presence of an excess of nitric acid or aqua regia amounting to ten per cent by volume of the liquid treated is not only not to be avoided in estimating barium as the sulphate, but is actually beneficial. Ordinarily the advantage is found in the tendency of the precipitate to fall coarsely crystalline under the conditions. In certain special cases in which certain substances mentioned, which would otherwise exert solvent action, are present, the precipitation is made complete. The contaminating effect of such substances when complete precipitation is induced may be corrected by dissolving the precipitate in sulphuric acid and recrystallizing by evaporation.

XXIV

ON THE TREATMENT OF BARIUM SULPHATE IN ANALYSIS.

By J. L. PHINNEY.*

In a recent paper by M. Ripper † entitled "Beiträge zur Gewichtsanalyse der Schwefelsäure" the method discussed is the precipitation of barium sulphate from an excess of the chloride, and differs from similar methods only in the manner of purification of the precipitate. Purification, according to Ripper, is accomplished by oxidizing with bromine water whatever sulphate may have been reduced by the ignition of the filter, then treating the entire precipitate with dilute hydrochloric acid until the impurities are removed. In the course of his investigation Ripper made the attempt to eliminate the possible source of error in the reduction of the sulphate by the use of the asbestos filter-crucible, but finding it impossible to bring asbestos to a sufficiently constant weight either by itself or when treated with dilute acid, he abandoned it as impracticable, and substituted the treatment of the reduced precipitate with bromine. Ripper accepts without investigation the old method of purifying barium sulphate by hydrochloric acid.

Inasmuch as the asbestos crucible has been employed successfully even in processes so delicate as atomic weight determinations, sufficient confidence was felt in it to warrant testing by its use the accuracy of the hydrochloric acid process of purification, in this way reducing the necessary manipulation and completely avoiding the introduction of bromine. Furthermore the recent work done in this labora-

* From Am. Jour. Sci., xlv, 468.

† Zeitschr. anorg. Chem., ii, 86.

tory by Mar and Browning* on barium sulphate depends for its validity upon the practical utility of this means of gathering and weighing barium sulphate. Accordingly the following preliminary series of experiments were undertaken with a view of discovering under what conditions and how far the asbestos crucible could be depended upon in quantitative methods as applied to the estimation of barium as sulphate. In Series I the crucible with a felt was ignited to bright redness for different periods of time and weighed, then washed with hydrochloric acid, both cold and hot, ignited, and re-weighed with results as shown below. The crucible used was finely perforated and furnished with a cover and cap, and the asbestos was prepared as directed by Gooch,† in his original paper. A felt weighing 0.0258 grm. was thrown upon the crucible, washed thoroughly with distilled water, dried, ignited, and weighed in less than twenty minutes. The formation of blisters due to rapid generation of steam was easily avoided by gradually increasing the temperature from a gentle heat. A second crucible with a felt weighing twice as much (0.0441 grm.) was ignited at low redness for equal periods with similar results.

SERIES I.

Time of ignition.	Weight in grams.	Time of ignition.	Weight in grams.
min.		min.	
2	0.0258	10	0.0258
2	0.0258	10	0.0258
2	0.0258	20	0.0258
5	0.0258	20	0.0258
5	0.0258	30	0.0258

The same felt was washed with 20 cm^3 of a twenty-five per cent solution of hydrochloric acid, then treated with 5 cm^3, 25 cm^3 cold, and 25 cm^3 hot concentrated acid respectively, and suffered in no case the slightest diminution in

* Am. Jour. Sci., xli, 288; xlv, 399. This volume, pp. 63, 181.

† Am. Chem. Jour., i, 317.

weight, constant weights being secured after an ignition of two minutes. Finally, as a matter of curiosity rather than because of its practical bearing, the felt was digested in the crucible for fifteen hours in concentrated acid, washed with 100 cm^3 distilled water, and even then lost but 0.0001 grm. The stability of the asbestos under the foregoing treatment is remarkable. An excessive ignition for nearly two hours at bright redness gave no appreciable change, while in the last experiment the trifling loss may perhaps be accounted for by mechanical disintegration.

SERIES II.

	$BaCl_2 . 2H_2O$ taken.	Time of ignition.	$BaSO_4$ found.	Error.	Treatment with acid.	Weight after treatment.	Loss.
	grm.	min.	grm.	grm.		grm.	grm.
(1)	0.5071	10 20	0.4848	0.0003+	4–5 drops HCl 4–5 drops HCl	0.4845 0.4845	0.0003 0.0000
(2)	0.5022	10 20	0.4799	0.0001+	4–5 drops HCl 4–5 drops HCl	0.4796 0.4793	0.0003 0.0003
(3)	0.5007	5 5	0.4783	0.0001–	100 cm^3 8 per cent HCl	0.4751 . . .	0.0032 . . .

In Series II, barium sulphate brought to a constant weight was treated with acid on the felt without difficulty — in the first two cases with a few drops of dilute hydrochloric acid followed by 10 cm^3 of distilled water, in the third with 100 cm^3 of a three per cent solution of the acid — though Ripper raises the further objection, that upon ignition the precipitate becomes so firmly attached to the felt that it is nearly or quite impossible to make a thorough treatment with acid. In experiments (1) and (2) no attempt was made to pulverize the precipitates, but in experiment (3), as also throughout Series III, on moistening with a few drops of water the sulphate was easily and completely disintegrated by a glass rod into finely divided particles. This difference in treatment explains, at least in part, the large difference in the results of the table.

The filtrates in experiment (2) gave with an excess of sulphuric acid slight unweighable precipitates, but from the

filtrate of experiment (3) 0.0030 grm. of the sulphate were recovered. The disintegrated residue from experiment (2) (0.4793 grm. $BaSO_4$) was next treated under precisely the same conditions as in the last preceding experiment, except that in this solution there was present dilute sulphuric acid amounting to five per cent of the entire volume, an excess sufficient to keep the barium in the form of sulphate.* In this case there was no loss in weight, nor did the filtrate contain any barium.

This work completely demonstrates not only that strong hydrochloric acid has no effect upon the film of asbestos, but also that barium sulphate when thrown upon it may be brought to a constant weight either by itself or after treatment with dilute acids, and incidentally that the requisite excess of sulphuric acid must be present to counteract the solvent effect of the hydrochloric acid. That Ripper failed to secure constant weights is probably due to unfamiliarity with the proper sort of material to be used.

In view of the facts thus far ascertained the next step was to purify the sulphate, if possible, by the means already referred to in the beginning of this paper. The contaminating salts chosen were potassium chlorate and sodium chloride, as those most likely to present a fair test of the efficacy of the process. The following precipitations were made:

No.	$BaCl_2 . 2H_2O$ taken.	$BaSO_4$ found.	Error.	Contaminating salt.
	grm.	grm.	grm.	grm.
1.	0.5008	0.5009	0.0224+	$KClO_3$, 3
2.	0.5014	0.4990	0.0198+	$KClO_3$, 3
3.	0.5007	0.4980	0.0196+	NaCl, 10
4.	0.5004	0.5165	0.0384+	NaCl, 20
5.	0.5012	0.4979	0.0190+	$KClO_3$, 3

By reference to the following table in which the records of treatment of these precipitates are given in their numerical order, it will be seen that the action of hydrochloric acid in

* Fresenius, Zeitschr. anal. Chem., xxx, 455.

the presence of sulphuric acid is to remove only from 70 to 90 per cent of the total impurity, and that, while it is possible by repeated treatments with dilute hydrochloric acid alone to so reduce the weight that there may be little or no apparent error on the original determination, the large percentage of sulphate dissolved at the same time condemns its use in accurate analytical work.

SERIES III.

No.	Acids used in total vol. of 100 cm³. HCl	H_2SO_4	Duration of acid treatment.	Loss on treatment.	Impurity remaining.	$BaSO_4$ recovered by H_2SO_4 in filtrate.
	cm³	cm³	min.	grm.	grm.	
1.	3	5	30	0.0175	0.0049	None.
	3	5	15	0.0012	0.0037	"
	3	5	15	0.0012	0.0025	Unweighable trace.
	3	5	15	0.0000	0.0025	" "
	3	5	15	0.0003	0.0022	" "
	3	0	15	0.0031	0.0009—	0.0020 grm.
2.	3	5	20	0.0135	0.0063	None.
	3	5	20	0.0015	0.0048	"
	3	5	20	0.0003	0.0045	"
3.	3	5	30	0.0090	0.0106	None.
	5	10	20	0.0013	0.0093	"
	10	10	20	0.0023	0.0070	"
	25	10	20	0.0002	0.0068	"
	50	10	15	0.0002	0.0066	"
4.	90	10	15	0.0260	0.0124	None.
	90	10	15	0.0009	0.0115	"
5.	3	0	30	0.0146	0.0044	0.0007 grm.
	3	0	30	0.0040	0.0004	0.0032 "

Fresenius states * that barium sulphate impure from sodium or potassium chlorates may be completely purified by igniting the precipitate, moistening thoroughly with hydrochloric acid, evaporating to dryness and extracting with water, and that chlorides of these elements bring about no contamination. However, in the above series of precipitations the inclusion by the sulphate of sodium chloride and potassium chloride (left on ignition) was very marked, and accordingly four new precipitations were made, two in the presence of 10 grm. of sodium chloride, and two with an equal amount of potassium

* Zeitschr. anal. Chem., ix, 62.

chloride as the contaminating salt, in order to test the degree of purification reached by Fresenius' process. The evaporation was made over a steam bath and hot water was used in washing. It was found an easy matter to remove the precipitates from the felts after ignition by breaking up the caked mass with a glass rod by a rotary motion and gently tapping the crucible. After extraction the residue was thrown back upon the same felt, ignited, and re-weighed with results as below:

I.				
$BaCl_2 . 2H_2O$ taken.	$BaSO_4 + NaCl$ found.	Impurity before treatment.	Loss on treatment.	Impurity remaining.
grm.	grm.	grm.	grm.	grm.
0.5000	0.4955	0.0177	0.0079	0.0098
0.5003	0.4973	0.0193	0.0100	0.0093
II.				
$BaCl_2 . 2H_2O$ taken.	$BaSO_4 + KCl$ found.	Impurity before treatment.	Loss on treatment.	Impurity remaining.
grm.	grm.	grm.	grm.	grm.
0.5033	0.5024	0.0215	0.0131	0.0084
0.5017	0.5071	0.0277	0.0189	0.0088

Under the most favorable conditions an average of 0.0090 grm. of the total impurity in a half-gram of the impure sulphate remained untouched, and in one case a retreatment diminished this amount by only 0.0004 grm. Slight precipitates were recovered from the filtrates of II, the first weighing 0.0001 grm. and the second unweighable.

We are forced, then, to the conclusion that alkaline chlorides do contaminate barium sulphate thrown down in the presence of an excess of sulphuric acid* and that the process of purifying by hydrochloric acid does not purify. It would seem therefore that the only good method for purification is either to fuse, according to Fresenius, with sodium carbonate, extract and reprecipitate as sulphate, or to evaporate from solution in concentrated sulphuric acid according to Mar.

* Mar, Am. Jour. Sci., xli, 288. This volume, p. 71.

XXV

ON THE IODOMETRIC DETERMINATION OF THE NITRATES.

By HIPPOLYTE GRUENER.*

De Koninck and Nihoul † describe a method for the iodometric determination of nitrates, in which the decomposition of the nitrates is effected by the action of gaseous hydrochloric acid, the gases evolved being passed into potassium iodide; but the method is a cumbersome one. In a former paper ‡ a method was described according to which nitrates were decomposed successfully and easily by a solution of manganous chloride in hydrochloric acid, the products of decomposition being passed into potassium iodide, and the liberated iodine titrated with sodium thiosulphate. The ease with which hydriodic acid has been applied in this laboratory as a reducing agent in the determination of arsenic, chloric and antimonic acids § has suggested its application for the same end to nitric acid, and the present paper is the account of attempts in this direction.

The Action of Phosphoric Acid and Potassium Iodide upon Nitrates. — The decomposition of the last traces of nitrates in presence of potassium iodide and sulphuric acid does not occur except at very great concentrations, and, as at great concentrations sulphuric acid in presence of hydriodic acid itself liberates iodine, the use of sirupy phosphoric acid to bring about the required decomposition naturally suggested itself. Various attempts to simplify the process while still

* From Am. Jour. Sci., xlvi, 42.

† Zeitschr. angew. Chem., 1890, 477.

‡ Gooch and Gruener: Am. Jour. Sci., xliv, 117. This volume, p. 132.

§ Am. Jour. Sci., xl, 66; xlii, 220; xlii, 213. This volume, pp. 30, 73, 82.

registering the amount of reduction by arsenic acid in the residue proved futile, and a distilling apparatus was found to be necessary. For this purpose a small retort was used, the neck of which was bent downward about two inches from the body, so that the retort itself might be tipped backward, allowing the unbent portion of the retort to run upward, thus guarding against loss from spattering. Into the tubulature of the retort was ground a glass tube drawn out at both ends to serve as a perforated stopper for the entrance of carbon dioxide. The neck was passed through a rubber stopper into a side-neck Erlenmeyer flask, the exit tube of which was prolonged and dropped into a side neck test tube used as a trap. The retort was covered with a simply contrived hood which kept the upper parts warm and prevented the iodine from settling anywhere. In the retort was placed the nitrate with an excess of potassium iodide, and in the receiver a known amount of decinormal solution of arsenious oxide strongly alkaline with hydrogen sodium carbonate and diluted to a convenient bulk. The trap contained nothing but water. The phosphoric acid used was at first 10 cm^3 of strong acid, specific gravity 1.7, with varying amounts of water, but when it was found that the amount of water present was an essential feature, a definite mixture was used as designated in the tables. The acid was added to the retort last of all, and after carbon dioxide had been passed for a sufficient length of time heat was applied. The carbon dioxide was evolved in a Bonn generator from materials which had been carefully boiled, and cuprous chloride was added to the acid in the generator to take up the oxygen from any traces of air. Between the introduction of phosphoric acid into the retort and the application of heat a good stream of gas was passed for ten minutes, at the end of which time the bubbles escaping at the last trap were completely absorbed in potassium hydrate of the requisite strength.

The first experiments were in blank with no nitrate present. Upon warming the mixture of phosphoric acid and 2 grm. of the iodide signs of free iodine were developed,

and by titration of the contents of the receiver at the end, iodine to the amount of 0.0014 grm. was found to have been liberated, either by residual traces of air or by dissociation. The experiment was repeated, but in this case all the water used had been boiled immediately before the experiment, and here iodine to the extent of 0.0009 grm. only was found to have been liberated. The cause and remedy for this liberation of iodine are discussed presently. A series of experiments was performed to study the action of the reagents when nitrates were present.

The method of procedure was as follows: The nitrate was taken for convenience from a solution of 5 grams in 500 cm^3 of water. The iodide was introduced dry or in solution according to the bulk of water allowable. This mixture was boiled a moment to drive out all air, the phosphoric acid was then added, and carbon dioxide was passed as described, the receiver containing the arsenious oxide and the trap being already in position. It had been found that all but a trace of iodine was caught in the first receiver, so that the rubber

TABLE I.

Exp.	KNO_3 taken.	KI taken.	Water added to 10 cm^3 of phosphoric acid, sp. gr. 1.7.	KNO_3 found.	Error in KNO_3.	Error in HNO_3.
Series 1.	grm.	grm.	cm^3	grm.	grm.	grm.
(1)	0.0005	0.2	2	0.0009	0.0004+	0.0002+
(2)	0.0010	0.2	2	0.0012	0.0002+	0.0001+
(3)	0.0020	0.2	2	0.0021	0.0001+	0.0001+
(4)	0.0050	0.2	2	0.0055	0.0005+	0.0003+
(5)	0.0100	0.2	2	0.0093	0.0007−	0.0004−
(6)	0.0100	0.2	2	0.0103	0.0003+	0.0002+
(7)	0.0200	0.3	3	0.0216	0.0016+	0.0010+
(8)	0.0200	0.3	3	0.0192	0.0008−	0.0005−
(9)	0.0200	0.3	3	0.0205	0.0005+	0.0003+
(10)	0.0200	0.3	3	0.0205	0.0005+	0.0003+
(11)	0.0500	0.5	6	0.0496	0.0004−	0.0002−
(12)	0.0500	0.5	6	0.0499	0.0001−	0.0001−
(13)	0.0300	0.5	4	0.0293	0.0007−	0.0004−
Series 2.						
(14)	0.0616	1.5	1	0.0682	0.0066+	0.0039+
(15)	0.0570	2.5	1	0.0643	0.0073+	0.0045+
(16)	0.1030	1.1	1	0.1061	0.0031+	0.0018+
(17)	0.1062	1.1	1	0.1197	0.0135+	0.0081+

stopper closing it could do no harm. When large amounts of nitrate were used the clots of solid iodine settling out in the receiver were dissolved by means of a crystal or two of potassium iodide. The solution in the retort was boiled until it was clear that all the iodine had distilled over, and usually until the boiling in the retort had ceased. It was found advisable to empty the retort so soon as it was cool enough, else the phosphoric acid became unmanageable. The retort after each experiment was washed out with ammonia and water.

The results of these first experiments are shown in Table I.

With one or two exceptions the results of Series 1 are fairly good. Those of Series 2 are very bad. The only essential difference between the two series is in the dilution of the phosphoric acid used. In the first series there is always enough water present to make the specific gravity of the phosphoric acid no higher than 1.6 for small amounts of iodide and nitrate, and lower than that number when these amounts are increased. The suggestion is obvious that dissociation of the hydriodic acid may occur at the boiling point of the stronger acid. According to Berthelot * aqueous solutions of hydriodic acid under pressure begin to dissociate at 275° or even under. The temperature of the retort at the end of an experiment was taken and found to be far beyond the range of a thermometer reading to 360°. It is evident, then, that under the conditions there should be opportunity for dissociation. Four experiments in which potassium iodide was treated with phosphoric acid, specific gravity 1.7, undiluted, gave of liberated iodine caught in arsenious acid 0.0030 grm., 0.0044 grm., 0.0049 grm., 0.0030 grm., corresponding to 0.0008 grm., 0.0012 grm., 0.0013 grm., 0.0008 grm. of potassium nitrate respectively. These results would account only in part for the errors noted, but they are in the same direction. Chapman † has found that concentrated hydriodic acid acting upon organic nitrates and nitrites reduces them not alone to nitric oxide but even in part to

* Ann. Chim., IV, xx, 392. † Jour. Chem. Soc., xx, 166.

ammonia. The conditions of the experiments in Series 2 approximate to concentration of the hydriodic acid, and the reaction that Chapman found probably takes place here to a limited extent. Concentration of the hydriodic acid then must be avoided, both to eliminate dissociation and excessive reduction of the nitrate.

Therefore the plan was adopted of diluting the solution, so that the temperature and concentration should be effective in decomposing the nitrate, but should not bring about the complications just mentioned. A blank experiment made thus, 18 cm^3 of a solution of phosphoric acid of specific gravity 1.39 being used, gave of liberated iodine only 0.0004 grm. corresponding to 0.0001 grm. of potassium nitrate. So that under these conditions we may be assured that dissociation occurs if at all to only a slight extent. In the following experiments, therefore, the nitrate is decomposed in presence of dilute phosphoric acid, the dilution and the quantity taken being included in Table II.

The iodine of (41) was collected in potassium iodide and titrated with thiosulphate. Series 3 requires little special comment. The experiments ran along smoothly, the manipulation was easy, the care required in watching very little, and the results are fairly satisfactory. The causes leading to the high results of Series 2 seem entirely eliminated by the dilution. Series 4 is a direct continuation of Series 3, differing in the single point that larger amounts of nitrate are handled. These results with some exceptions are decidedly low. It appears that with a fair percentage of water present, as the amounts of nitrate grew larger, the error became a negative one. The explanation for this seemed to be that the last portions of nitric acid must have distilled before decomposition, whenever the original amount was large. Nitric acid was accordingly tested for in the distillate, and to this end all the conditions of the experiment were repeated, except that the receiver contained only water. Of the nitrate 0.4 grm. and of the iodide 4 grm., twice the amount theoretically necessary, were put into the retort, and at the end of

the experiment the solution in the receiver was boiled with hydrogen peroxide to decompose the hydriodic acid and drive out the iodine, care being taken to keep enough water to hold any nitric acid present. When all the iodine was gone sodium carbonate was added, the solution evaporated, and the residue ignited and tested with a saturated solution of manganous chloride in hydrochloric acid, as described in the previous paper above mentioned. By this means 0.0002 grm. potassium nitrate are very easily detected in 10 cm^3 of solution. Nitric acid was found in the distillate of this experiment as well as in two others conducted with 0.2 grm. and 0.1 grm. of the nitrate respectively. The residues in the retorts of these three tests showed no trace of nitric acid.

TABLE II.

	KNO_3 taken.	KI taken.	Found.	Sp. Gr. of solution of phosphoric acid.	Amount of sol. used.	Error KNO_3	Error HNO_3
Series 3.	grm.	grm.	grm.		cm^3	grm.	grm.
(18)	0.0500	1.	0.0500	1.43	17	0.0000	0.0000
(19)	0.0200	0.5	0.0201	1.43	17	0.0001+	0.0001+
(20)	0.0200	1.	0.0198	1.43	17	0.0002−	0.0001−
(21)	0.0250	1.	0.0250	1.42	17	0.0000	0.0000
(22)	0.0300	1.	0.0307	1.43	17	0.0007+	0.0004+
(23)	0.0300	1.	0.0312	1.43	17	0.0012+	0.0007+
(24)	0.0350	1.	0.0353	1.43	17	0.0003+	0.0002+
(25)	0.0400	1.	0.0409	1.35	20	0.0009+	0.0006+
(26)	0.0450	1.	0.0444	1.35	20	0.0006−	0.0004−
(27)	0.0500	1.	0.0499	1.37	20	0.0001−	0.0001−
Series 4.							
(28)	0.0600	1.	0.0568	1.37	20	0.0032−	
(29)	0.0600	1.	0.0575	1.37	20	0.0025−	
(30)	0.0600	1.	0.0576	1.37	20	0.0024−	
(31)	0.0600	2.	0.0588	1.37	20	0.0012−	
(32)	0.0600	2.	0.0605	1.37	18	0.0005+	
(33)	0.0700	2.	0.0708	1.37	18	0.0008+	
(34)	0.0800	2.	0.0811	1.37	18	0.0011+	
(35)	0.0900	2.	0.0842	1.37	18	0.0058−	
(36)	0.1000	2.	0.0996	1.37	18	0.0004−	
(37)	0.1000	2.	0.1012	1.37	18	0.0012+	
(38)	0.1000	1.5	0.0909	1.37	18	0.0091−	
(39)	0.1000	2.5	0.0979	1.37	18	0.0021−	
(40)	0.1021	3.	0.1005	1.43	17	0.0016−	
(41)	0.1032	2.	0.0949	1.43	17	0.0085−	

The process seems reliable enough, then, for estimating nitrates in small quantities not exceeding an equivalent of

0.04 grm. or 0.05 grm. of potassium nitrate. Every experiment performed with quantities not larger than 0.05 grm. has been given here, except four in which an imperfection in the apparatus showed an obvious mechanical loss. The errors in these experiments lie between the extremes of 0.0016 grm. + and 0.0008 grm. — on the nitrate, with an average error of 0.00016 grm. If series 3 alone is taken, in which the dilution of the phosphoric acid was regulated, we have as extreme errors 0.0012 grm. + and 0.0006 grm. — with a mean error of 0.0002 grm. +. With quantities of nitrate above 0.05 grm. the process does not seem a safe one, inasmuch as with a moderate amount of water present some nitric acid distils over undecomposed, and with little water present other complications as seen above arise.

The method so far as it is applicable may be summed up as follows. The nitrate, not to exceed in amount 0.05 grm. of potassium nitrate, is introduced into a retort, together with ten times its weight of potassium iodide, and 17 to 20 cm^3 of phosphoric acid, of specific gravity 1.43. All water used should be recently boiled. Carbon dioxide is passed from a receiver carefully set up. The neck of the retort passes into a receiver containing a known amount of decinormal arsenious oxide, alkaline with a good excess of hydrogen sodium carbonate and diluted to a convenient bulk. To this flask is attached for additional safety a simple trap containing water. The solution in the retort is boiled until it is clear that no more iodine remains, when the receiver, after proper washing and addition of the liquid in the trap, is titrated with iodine to find the amount of arsenious oxide still left. This gives the measure of the iodine evolved and consequently of the nitrate present, according to the equation

$$2HNO_3 + 6HI = 4H_2O + 2NO + 3I\text{–}I.$$

The Decomposition of Nitrates by Antimonious Chloride. — The failure mentioned above, in attempting to use arsenious oxide to register the action of nitric acid, led to the trial of antimonious chloride as a substitute, inasmuch as this sub-

stance is easily oxidizable and less volatile than arsenious chloride in presence of hydrochloric acid. This latter fact is of great importance in the decomposition of a nitrate. The point to be tested was whether the complete decomposition of nitrates by the action of antimonious chloride in hydrochloric acid solution, and the absorption of the nascent oxygen to form antimonic chloride would be secured, so that the antimonious chloride left at the end as compared with the amount taken should give the measure of the nitrate used, according to the equation

$$3SbCl_3 + 2HNO_3 + 6HCl = 3SbCl_5 + 2NO + 4H_2O.$$

Antimony chloride was dissolved in strong hydrochloric acid, and the solution standardized by diluting convenient portions, adding tartaric acid, nearly neutralizing with a 25 per cent solution of sodium hydrate, treating with excess of hydrogen sodium carbonate and titrating with decinormal solution of iodine in presence of starch, the blue color being taken as the end reaction.

Known portions of this solution boiled with potassium nitrate for a considerable length of time, then diluted, neutralized, and titrated (all a simple quick process), showed oxidation to the extent of about 90 per cent of the nitrate present. The evidence pointed to the conclusion that the nitrate was broken up, but that the residue failed to register the amount of decomposition. The products of decomposition when passed in a current of carbon dioxide into potassium iodide set free iodine, but had no oxidizing effect upon an alkaline solution of arsenious oxide. The conclusion was drawn that nitrosyl chloride was probably given off, which breaking up on contact with water into hydrochloric and nitrous acids exerts no effect upon arsenious oxide in alkaline solution. To see if the nitrosyl chloride was set free in exact measure of the nitric acid lost, the following experiments were made.

Into a diminutive retort — made from a pipette shaped like a Liebig's drier and connected by a sliding joint covered by

rubber into a Kjehdahl tube used as a receiver, and so placed that carbon dioxide passing through the apparatus should enter from below, lifting the air before it — the dry nitrate was introduced and washed down with a few drops of recently boiled water, or, if more liquid was required, with hydrochloric acid lest the liquid become too dilute. From a burette a definite amount of antimonious chloride solution, somewhat in excess of the nitrate taken, was introduced. The receiver was charged with 0.25 grm. potassium iodide diluted

SERIES I.

Exp.	KNO_3 taken.	KNO_3 corresponding to I found in receiver.	Entire KNO_3 found.	Error in KNO_3.	Error in HNO_3.
	grm.	grm.	grm.	grm.	grm.
(1)	0.0222	0.0020	0.0233	0.0011+	0.0007+
(2)	0.0336	0.0026	0.0333	0.0003—	0.0002—
(3)	0.0470	0.0045	0.0471	0.0001+	0.0001+
(4)	0.0553	0.0057	0.0554	0.0001+	0.0001+
(5)	0.0664	0.0076	0.0679	0.0015+	0.0009+
(6)	0.0759	0.0082	0.0752	0.0007—	0.0004—
(7)	0.0837	0.0103	0.0841	0.0004+	0.0002+
(8)	0.0934	0.0113	0.0955	0.0021+	0.0013+
(9)	0.1034	0.0134	0.1036	0.0002+	0.0001+
(10)	0.0262	0.0024	0.0259	0.0003—	0.0002—
(11)	0.0127	0.0007	0.0130	0.0003+	0 0002+
(12)	0.0065	0.0003	0.0067	0.0002+	0.0001+
(13)	0.0026	0.0001	0.0023	0.0003—	0.0002—
(14)	0.1232	0.0098	0.1227	0.0005—	0.0003—
(15)	0.1540	0.0146	0.1540	0.0000	0.0000
(16)	0.1878	0.0210	0.1865	0.0013—	0.0008—

with recently boiled water and was joined to a trap filled with water. After carbon dioxide had been passed through the apparatus for about ten minutes, the solution was warmed on a high boiling bath (103°–107°) to ensure the safety of the retort, to keep the antimony pentachloride from breaking up, to retain the bulk of the acid in the retort, and to prevent mechanical loss. This method of proceeding was found entirely satisfactory. After fifteen minutes' digestion the receiver and trap were washed out and at once titrated with sodium thiosulphate. The residue in the retort was treated exactly as was the antimonious chloride when it was standardized. The solution here must be kept dilute, lest at

the great heat caused by neutralizing strong solutions there be action upon the pentachloride on the part of the small amount of tartaric acid now present. The difference between the iodine required to oxidize the trichloride left in the retort and the iodine found in the receiver is the measure of trichloride left unoxidized by the nitrate, and by difference we have the measure of the nitrate present. The results are given in Series I. In experiments (1) to (8) the receivers were washed with ordinary distilled water; after that with water recently boiled.

SERIES II.

Exp.	KNO_3 taken.	KNO_3 corresponding to I found in receiver.	Entire KNO_3 found.	Error in KNO_3.	Error in HNO_3.
	grm.	grm.	grm.	grm.	grm.
(17)	0.0530	0.0052	0.0533	0.0003+	0.0002+
(18)	0.0547	0.0065	0.0549	0.0002+	0.0001+
(19)	0.0541	0.0063	0.0537	0.0004—	0.0002—

The experiments of Series II were performed to see if the titration of the iodine set free in the receiver could be accomplished as well in alkaline solution by means of arsenious oxide. For this purpose the solutions from the receivers were poured into a strong solution of sodium bicarbonate, care being taken to prevent loss during effervescence.

The results run from extremes of .0021 grm. + to .0013 grm. — with a mean error of .00016 grm. +, which tends to emphasize the well-known fact that it is impossible to remove every trace of air from reagents and generator. The operation is quick, taking in all three-quarters of an hour and requiring very little watching. The experiments given are all that were performed with the apparatus as described, it not having been found necessary to reject a single determination for mechanical mischances.

The processes described do not in general present advantages equal to those of the manganous chloride method to which reference has been made, but under special conditions they may be found useful.

XXVI

ON THE REDUCTION OF NITRIC ACID BY FERROUS SALTS.

By CHARLOTTE F. ROBERTS.*

Among the most common methods for the estimation of nitric acid are those which depend upon its reduction by a ferrous salt in acid solution. The amount of the nitrate acted upon is reckoned either from the oxidation of this ferrous compound or from the nitric oxide set free and subsequently determined. The first-named method was first put in practical form by Pelouze, and in its present modified form,† is capable of yielding accurate results in the analysis of pure nitrates. Organic matter interferes, however, with the accuracy of the indications of Pelouze's process. Schloesing‡ was the first to use the nitric oxide evolved as a measure of the original nitrate, and he was able to show that the presence of organic matter does not influence the yield of nitric oxide in the decomposition. Schloesing originally estimated the nitric oxide by collection over mercury, re-conversion by the action of oxygen to nitric acid, and titration of the last with standard alkali, but Reichardt,§ Wildt and Scheibe,‖ and others have very much simplified the apparatus of the original process, and shown that the gas may be collected over caustic soda or potash without materially diminishing the accuracy of the analytical process. Schulze and Wulfert¶ determined by direct measurement the nitric oxide

* From Am. Jour. Sci., xlvi, 126.
† Fresenius, Quant. Anal., 6. Aufl., p. 519.
‡ Ann. Chim. III, xl, 479.
§ Zeitschr. anal. Chem., ix, 26.
‖ Zeitschr. anal. Chem., xxiii, 151.
¶ Zeitschr. anal. Chem., ix, 400.

collected over mercury, and Tiemann showed that the determination loses little in exactness when the gas is measured over an aqueous solution of caustic soda.

Many modifications and extensions of these processes have appeared from time to time, the detailed consideration of which is not essential to the purpose of the present discussion, but all, whether dependent upon the determination of the change of condition of the iron salt in the residue, or upon the estimation of the nitric oxide evolved, rest upon the assumption that under the conditions of action nitric oxide is the sole reduction product in the complete destruction of the nitric acid by the ferrous salt. That this assumption is true in the main is evidenced by the analytical results of the methods. Thus, in his careful and critical examination of methods, Eder* found that the indications given by titration of the residue of treatment with ferrous chloride and hydrochloric acid by means of potassium permanganate showed errors of excessive oxidation amounting only to 0.3 per cent to 1 per cent upon amounts approximating 0.4 grms. of potassium nitrate, although the process involved the uncertainties of titrating, without the now used precautions, with permanganate in hydrochloric acid. The similar process in which use is made of ferrous sulphate in sulphuric acid, instead of the chloride in hydrochloric acid, gave excellent results and showed errors of loss of the nitrate ranging from 0.05 per cent to 0.4 per cent upon similar amounts of the nitrate, while Braun's process of determining the oxidized iron by stannous chloride gave upon amounts of the nitrate varying from 0.16 grms. to 0.32 grms. errors of 0.3 per cent to 1.5 per cent.

In the processes involving the treatment of the nitric oxide, the errors are usually greater and more variable. Thus, Schloesing's process gave Eder errors of 0.2 per cent to 2 per cent upon approximately 0.15 grms. of the nitrate, and 10 per cent and 12.5 per cent respectively upon 0.0279 grms. and 0.0249 grms. of the nitrate. In Reichardt's modification the

* Zeitschr. anal. Chem., xvi, 267.

errors are slightly larger on the average but vary similarly, and Tiemann's method of measuring the gas over caustic soda yields results closely comparable with those of the Reichardt process and but little inferior to those of Schloesing.

The way in which the results vary in all the processes in which the nitric oxide is estimated has very generally been regarded as suggestive of an oxidizing action upon the nitric oxide, nearly constant in amount, and productive of increasing percentage errors as the amount of nitrate decreases. The intermixture of ordinary air would naturally produce diminution of the volume of the nitric oxide, but the oxidation of this by free air of normal composition should produce no effect upon the total volume of the gas in cases where this is measured, if the oxidation goes, as is generally supposed to the point of forming nitrous acid; for the introduction of a given volume of oxygen (in air) means the simultaneous introduction of four volumes of nitrogen, and the single volume of oxygen is capable of causing the disappearance of exactly four volumes of nitric oxide, converting it into nitrous acid, so that four volumes of nitrogen would be left to replace the four volumes of nitric oxide removed. If the oxidation be supposed to go to the point of forming some nitric acid there should be left three volumes of nitrogen to replace every volume of nitric oxide converted to nitric acid, and the total volume should be greater after oxidation than before.

In order to account for the low results, therefore, on the assumption of an oxidizing action due to free air, we must conclude that such air is derived principally from solution in the reagents, which would naturally hold oxygen in excess of the proportion in which it exists in atmospheric air. Air in solution in the receivers would most readily produce the observed decrease in volume, for the nitrogen in dissolved air would naturally still remain dissolved without relation to the disappearance of dissolved oxygen. If the deficiencies observed in Schloesing's process are due at all to oxidation of the nitric oxide, it is natural to suppose that such oxidation

must take place during the passage of the gas from the evolution flask to the mercurial receiver, but in the processes which involve the collection of the gas over aqueous caustic alkali oxidation might readily be brought about by dissolved oxygen, and in this case the nitric oxide removed would not be replaced by nitrogen. The last mentioned source of error, Glaser * has recently proposed to correct by collecting the gas over a solution of potassium iodide instead of over caustic soda.

The deficiency in the total volume of gas may also be caused partially or wholly by the solubility of nitric oxide in caustic alkali. Warington † has shown that caustic soda is capable of slowly absorbing nitric oxide, and Russell and Lapraik ‡ state that upon long standing over caustic soda, nitric oxide is decomposed into nitrous acid, nitrous oxide, and nitrogen.

Errors of the same sort and in the same direction as those produced by the action of caustic alkali, either alone or with dissolved air, or of air in the apparatus, would be the natural consequence of a failure of the ferrous salt to effect decomposition exactly according to the assumed reaction. Incompleteness of decomposition of the nitric acid; or the formation of an oxide of nitrogen higher than nitric oxide would result in producing too small a volume of nitric oxide, and so also would the over reduction of the nitric oxide to nitrous oxide or nitrogen. We have, moreover, abundant evidence on the one hand both of the incompleteness of decomposition of nitric acid and of the production of a higher oxidation product by the action of the ferrous salt under modified conditions, and, on the other hand, the statement of Carius § that prolonged contact of nitric oxide with ferrous sulphate induces further reduction of the nitric oxide. Thus, Abel and Bloxam ‖ found that when the nitrate was introduced into a boiling solution of ferrous

* Zeitschr. anal. Chem., xxxi, 285. † Jour. Chem. Soc., xxxvii, 476.
‡ Jour. Chem. Soc., xxxii, 35. § Ann. Chem. Pharm., xciv, 138.
‖ Jour. Chem. Soc., ix, 97.

sulphate containing an excess of sulphuric acid, nitrous acid was evolved, and some nitric acid remained unaltered even after prolonged boiling; and Eder,* after demonstrating (at least inferentially from analytical results) that practically complete decomposition to nitric oxide results when the nitrate is put into a strongly acid and cold solution of ferrous sulphate in excess, and the heating made gradual, showed that under conditions otherwise similar excepting that the mixture was *boiling* when the nitrate was introduced, a higher oxide of nitrogen was evolved in quantity sufficient to be visibly red, while the oxidation of the ferrous salt in the residue fell to ninety per cent of its normal value.

These facts and the consideration that the analytical methods in which the nitric oxide is estimated give without exception unexpectedly low results have led me to look a little more carefully into the conditions under which the reaction of ferrous salts upon the nitrate may be expected to give the volume of nitric oxide most nearly approaching the theoretical yield.

The apparatus which I have found most satisfactory for this work consists of a small tubulated retort, upon the neck of which is fitted a small condenser to prevent loss of liquid during the distillation. Into the tubulature of this retort is fitted tightly, by a carefully ground joint, a tube drawn out so as to dip below the surface of the liquid, and fitted with carefully ground stop-cocks, — as shown in the figure, — and so branched above as to make it possible to transmit carbon dioxide through the apparatus, or to admit any liquid without admixture of air. The condenser is joined to a Will and Varrentrapp bulb used as a trap, and this in turn is connected by thick vacuum tubing with a Hempel gas-burette. Carbon dioxide was generated in a Kipp's apparatus by action of boiled hydrochloric acid upon boiled marble, and the liquid was charged with cuprous chloride, following Warington's device, to take up traces of dissolved oxygen. Notwithstanding all precautions, I have met with the generally

* Zeitschr. anal. Chem., xvi, 267.

recognized experience in finding that the gas from the generator is never so pure that a hundred cubic centimeters of it will not leave a tiny bubble when shaken with a solution of caustic soda.

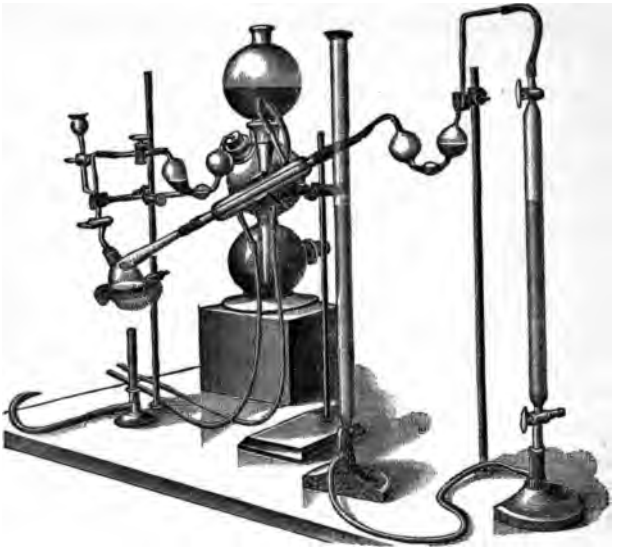


FIG. 8.

With the apparatus described the following experiments were made. Potassium nitrate (0.1 grm.) was introduced into the retort, generally in the dry condition, carbon dioxide was passed through the apparatus until the gas collected over sodium hydroxide left only the minute bubble which the gas from the generator alone had been found to give, and 40 cubic centimeters of a boiled solution of ferrous chloride in hydrochloric acid was admitted through the funnel tube, after shutting off the carbon dioxide and lowering the levelling tube of the Hempel burette. With the stop-cocks arranged as in sketch, the liquid was then slowly heated to boiling and the process continued until the reaction of the ferrous salt upon the nitrate was apparently complete, when the carbon dioxide was again passed through the apparatus to secure complete

removal of the nitric oxide, the absorption of the carbon dioxide being hastened by inclining and shaking the burette at intervals. The volume of the gas under existing barometric and thermometric conditions was noted. To discover how much of the gas collected was actually nitric oxide, I have found it best to absorb this gas by potassium permanganate. This is very easily and quickly accomplished by attaching a funnel to the Hempel burette through which a strong solution of potassium permanganate can be introduced. I have generally taken the precaution of adding water first in order to prevent the possibility of any local action between the potassium permanganate and caustic soda by means of which oxygen might be produced.

The following tables give the results of experiments performed in this way. In the first column is given the absolute volume of the gas unabsorbed by the permanganate, in the second the per cent potassium nitrate reckoned as if the total

Exp.	Vol. of unabsorbed gas.	Per cent from total vol.	Per cent from absorbed vol.	Iodine.
	I. With potassium iodide in the Will and Varrentrapp tube.			
	cm^3			grm.
(1)	0.45	99.98	98.1	0.0004
(2)	0.65	99.83	96.74	0.0008
(3)	0.45	100.3	97.6	0.0004
(4)	0.6	99.7	97.7	0.0022
	II. With water in Will and Varrentrapp tube.			
(1)	0.6	97.76	95.0	. . .
(2)	0.6	97.76	95.2	. . .
(3)	0.6	97.9	95.2	. . .
(4)	0.6	97.4	94.7	. . .
(5)	2.43	97.3	87.0	. . .

volume were nitric oxide, and in the third the percentage reckoned from the absorbed nitric oxide. In cases where potassium iodide was used in the Will and Varrentrapp tube

to break up any higher oxides of nitrogen that might be formed, the amount of iodine thus set free is given.

In experiment (3) of Table I, the ferrous chloride was made by dissolving iron wire in boiled hydrochloric acid, and the potassium nitrate was dissolved in boiled water and added to the ferrous chloride. With this dilution, the reaction proceeded very slowly and it was found necessary to add several successive portions of hydrochloric acid before the reaction was complete, but the results as finally obtained are quite comparable with those obtained by a more rapid process.

It will be seen by a glance at the tables that the best analytical results are obtained by the use of potassium iodide in the Will and Varrentrapp tube and calculation from the total volume of gas. The average of the results obtained above, omitting for a reason which will appear later the last experiment of the second series, may be expressed in this way:

	With KI.	With water.	Difference.
Per cent from total gas . . .	99.95	97.7	2.25
" " nitric oxide . .	97.53	95.0	2.53
Diff. . .	2.42	2.7	

In each case there is an amount of gas equal to about 2.5 per cent of the total volume which is not nitric oxide. In whichever way reckoned the total amount of gas collected is about 2.5 per cent greater when potassium iodide is used than when water is used in the Will and Varrentrapp tube. This would indicate that some higher oxide of nitrogen is formed and is decomposed by the potassium iodide with a liberation of nitric oxide equal to about 2.5 per cent of the total volume of gas. In case the formation of this oxide were due to traces of air which oxidized the nitric oxide to nitrous acid, the volume of nitrogen thus left would be, as has been shown, exactly equal to that of the nitric oxide oxidized, and therefore there should be about 2.5 per cent of gas incapable of absorption by potassium permanganate, which is practically found to be the case. This would furnish, then, a simple explanation of the results given. Supposing this explanation to be the

correct one, the presence of air should not influence the total volume of gas in case potassium iodide is not used. To test this point, the last experiment of the second series was performed. This experiment was done in exactly the same way as the others, except that the carbon dioxide was not allowed to pass through long enough to displace the air completely. It will be observed that the total volume of gas is practically the same as in the other experiments, but, as would naturally be expected, the volume of gas incapable of absorption by potassium permanganate is much increased.

An interesting confirmation of the supposition that small quantities of air introduced into nitric oxide confined over caustic soda would not influence the total volume of gas was found in some experiments performed later. After the nitric oxide in the Hempel burette had been accurately measured, air was introduced through the upper stop-cock, a cubic centimeter at a time, and the burette lightly shaken. It was found that more than twenty cubic centimeters of air could be introduced in this way without materially affecting the total volume of gas, but that the volume began to increase when about one cubic centimeter of nitric oxide was left unoxidized, as subsequently determined by potassium permanganate.

In the fifth experiment of Table II, supposing the 2.43 cubic centimeters of unabsorbed gas to represent nitrogen left from air which had oxidized the nitric oxide to nitrous acid 2.5 cubic centimeters of nitric oxide would thus have been made to disappear, and the amount of nitric oxide left should be 89 per cent, 2 per cent higher than that obtained. On the same supposition, in the four preceding experiments, the 0.6 cubic centimeters of unabsorbed gas represent a loss of 0.6 cubic centimeters of nitric oxide which corresponds to a loss of about 3 per cent on the nitrate, so that the results reckoned from the absorbed gas should be about 97 per cent instead of 95 per cent as found. Here, again, is an unexplained loss of about 2 per cent. Moreover, with the use of potassium iodide,

it is plain that, in whatever way these higher oxides of nitrogen may be formed, they should be entirely broken up into nitric oxide, so that the amount reckoned from the absorbed gas should be 100 per cent, whatever the total volume may be. We find instead that we get an average of 97.6 per cent, a loss of a little more than 2 per cent. It seemed probable, then, that as these experiments were done, there was a loss of from 2 to 2.5 per cent of nitric oxide by solution in caustic soda. This loss would mean the solution of 0.5 to 0.6 cubic centimeters of the gas after being thoroughly shaken with about 75 cubic centimeters of strong caustic soda, an amount of solubility which did not seem at all improbable and which would be quite in accordance with the results of Warington's experiments, previously mentioned.

The following set of experiments was therefore undertaken with the double object of studying the solubility of nitric oxide in caustic soda, and noting any conditions of temperature or proportions which might influence the course of the reaction. The same apparatus was used as in the preceding experiments, except that a Geissler tube filled with water was inserted between the Will and Varrentrapp tube and the Hempel burette to prevent the possibility of any iodine being carried over mechanically into the gas receiver. In all cases the Will and Varrentrapp tube was filled with potassium iodide, and the amount of iodine liberated estimated by titration with sodium thiosulphate.

III.

	Per cent reckoned from total vol. of gas.	Amount of iodine in grams.
(1)	99.	0.0024
(2)	100.5	0.0043
(3)	99.2	0.0150
(4)	99.4	0.0020
(5)	100.8	0.00355
(6)	98.9	0.0008

In the last five experiments of this series, the caustic soda solution was thoroughly boiled to eliminate any error which

might arise from oxidation of the nitric oxide by air dissolved in the liquid, but with no marked difference in the results.

In all except the last one of these experiments, the nitrate and ferrous chloride were brought together in a more or less hot solution instead of being heated gradually, and although the amounts of iodine vary, it will be seen that they are on the whole greater in this series than in the experiments in which the reacting bodies were brought together in the cold. This would indicate the possibility of some slight local action in the hot solution by which higher oxides of nitrogen are generated, but any analytical error from this source is corrected by the use of the potassium iodide which converts them into nitric oxide.

In experiment (3) of this series, where a very large amount of iodine is liberated, only one half as much ferrous chloride was used in proportion to the amount of nitrate as was taken in the other experiments, so that the amount of iron present must have been very near the theoretical limit. Here the amount of iodine would indicate the formation of a higher oxide of nitrogen, an error corrected however by the use of potassium iodide so that the percentage as calculated from the total volume of gas compares well with the results obtained in the other experiments. In experiment (6) also, a rather small excess of the $FeCl_2$ was taken (0.255 grms. Fe being weighed out, whereas 0.168 is theoretically required), but in this case the liquids were almost cold when brought together, and the amount of iodine set free is very small.

In several cases experiments were made to test the solubility of the nitric oxide in caustic soda. In experiment (2) the gas was allowed to stand over the liquid, with frequent shaking, for about an hour when the volume had decreased from 24.8 to 22.6 cubic centimeters. In experiment (3), after the lapse of an hour with similar treatment, the volume of gas had decreased four cubic centimeters, and one cubic centimeter was lost by the gas simply standing over night over caustic soda.

To determine whether the nitric oxide went into solution as

such or in the form of nitrite, the following experiments were performed. About 30 cubic centimeters of the liquid were drawn off by stop-cock at bottom of Hempel's burette into an acidified solution of potassium iodide, freely exposed to air, and the amount of iodine set free determined by titration with sodium thiosulphate. Again, 30 cubic centimeters more of the same solution were treated in exactly the same way except that the flask containing the potassium iodide was first filled up with carbon dioxide and air carefully excluded. On two trials it was found that the amount of iodine set free under the latter circumstances was very small, and less than one-half as much as that set free when air was admitted freely, showing very plainly that some, and perhaps most, of the nitric oxide was dissolved as such, without chemical action of the caustic soda.

The principal conclusions to which this study of the estimation of nitrates, by measurement of the volume of nitric oxide swept along by carbon dioxide and collected over caustic soda, has led me, are as follows:

1. The best analytical results are obtained according to this method by passing the gas through potassium iodide before collection, and estimating from the total volume of gas collected.*

2. If air be present in the apparatus at the outset, it will not affect the total volume of gas if potassium iodide be not used, or if the nitric oxide meet the air beyond the Will and Varrentrapp bulb. When potassium iodide is used, air in the apparatus would make the total volume too large, but with small amounts of air, this error is counterbalanced by the solubility of nitric oxide in caustic soda.

3. Since the nitric oxide is perceptibly soluble in caustic soda upon shaking, the gas should not be left long in contact with the liquid before the volume is measured.

4. If the hydrochloric acid used is very dilute, the reaction proceeds very slowly, but leads finally to the same results.

* This result accords with Glaser's experience in collecting the gases evolved unmixed with CO_2, over KI—[loc. cit.].

5. If the nitrate and ferrous salts are brought together hot, some higher oxides of nitrogen may be formed, but the error is corrected by the use of potassium iodide.

6. If potassium iodide is used the results are accurate even when the ferrous chloride is present only in very slight excess.

XXVII

THE STABILITY OF STANDARD SOLUTIONS OF TARTAR EMETIC.

By HIPPOLYTE GRUENER.*

During the progress of some investigations on antimony, I found it desirable to know to what extent a solution of tartar emetic could be relied on to retain its strength when kept for a length of time. Accordingly I made up a number of solutions of tartar emetic, whose strength was determined by titration in presence of an alkaline tartrate and bicarbonate with decinormal iodine, standardized against arsenious oxide. These solutions were put aside in stoppered bottles for a number of months, when they were again determined with iodine standardized against the same arsenious oxide.

Solution A was simply tartar emetic in distilled water, 16 grms. to the liter. At the end of five months this was found to have lost strength to a considerable extent, while a deposit, seemingly a mixture of antimonious oxide and of fungus growth had settled at the bottom of the bottle. At the end of fourteen months a still greater loss of strength was observed, corresponding in all to about 3.5 per cent of the tartar emetic, of which 4 grms. were present. The sediment was drained, dissolved in tartaric acid and titrated with iodine. It was found to correspond to 0.13 grm. of tartar emetic or approximately the amount lost. This shows clearly that under the conditions no great loss is caused by the formation of the pentoxide, in closed bottles at least.

Solution B was slightly alkaline with sodium bicarbonate in presence of sodium tartrate. On this solution after five months there was developed in addition to a fungus growth a deposit, probably antimonious oxide; there was here a slight

* From Am. Jour. Sci., xlvi, 206.

loss in the strength of the solution, amounting to 1 per cent.

Solution C was acid with tartaric acid only. After ten months the solution was found of the same strength and clearness as it was originally: but four months later there was a slight deposit accompanied by a loss of 1.2 per cent.

Parallel experiments to A gave like results. Two repetitions of C with varying amounts of tartaric acid present showed in each case a decided fungus growth with no loss of strength at the end of five months, whereas at the end of nine months the loss amounted to 1 per cent for the larger amount of tartaric acid and 0.3 per cent for the smaller amount.

It seems then that there is little danger of any oxidation of the antimonious oxide occurring, and provided enough tartaric acid is present to keep all the antimonious oxide in solution, the solution should maintain its strength for at least five or six months. The fungus growth has not been found to interfere in practical work with the solutions, yet it seemed advisable to prevent its formation if it could be done simply. To test the possibility of this, a number of solutions were prepared containing varying amounts of hydrochloric acid, which should act as a sterilizer; enough tartaric acid was added to counteract any tendency toward precipitation. In one series of experiments the solutions were sterilized at the beginning by boiling; in the other series distilled water which had been exposed more or less to the air for a number of days was directly used. Where the solutions had been thus sterilized no sign of fungus growth had appeared at the end of five months, and in the case of the unsterilized solutions there was never more than a trace. Where the hydrochloric acid present was not more than 10 cm^3 to 500 cm^3 of water, there was at the end of three months only the faintest trace of a deposit and no material loss of strength. Where the hydrochloric acid was present to the extent of 25 cm^3 in 500 cm^3 of water a decided granular precipitate was observed, accompanied by a loss of strength of about 10 per cent. The granular pre-

cipitate when dissolved in tartaric acid and titrated accounted almost exactly for this loss.

A number of solutions were prepared under varying conditions and left open to the air for three months, at the end of which time no loss from oxidation was found.

It may be seen that tartar emetic in a solution of 16 grms. to the liter is not oxidized either in closed or open bottles. If it is desired to keep this solution as a standard for a moderate length of time it can be done in presence of enough tartaric acid (20 to 30 grms. to the liter) to prevent precipitation. The addition of 1 cm^3 hydrochloric acid to one liter of solution is enough to prevent any decided formation of fungus growth, at the same time not enough to cause a deposit as happens when large amounts of hydrochloric acid are used.

In the titration of tartar emetic in presence of starch the permanent blue color was taken in every case as the indication of the end reaction, as all other shades of color were found unsatisfactory. It is a well known fact that in the titration of antimony salts the color of the starch iodide is not developed until there is a considerable excess of iodine present, so that as compared with arsenious oxide, iodine gives high results with antimony. Thus, for example, the mean of six series of determinations made at various times and aggregating twenty-nine determinations showed the presence of 43.95 per cent of antimonious oxide in tartar emetic. (Sb = 120 and tartar emetic $KSbOC_4H_4O_6 . \frac{1}{2}H_2O$. = 332, requiring 43.37 per cent.)

The facts above shown, that tartar emetic may be kept in stable solution by means of tartaric acid and hydrochloric acid in the proportions given, make it possible to use and keep such solutions for standardizing iodine for the determination of antimony, and thus to eliminate the error due to the tardy development of the starch iodide blue in presence of antimony salts, observed when compared arsenious oxide is used as a standard.

XXVIII

ON THE ESTIMATION OF CHLORATES AND NITRATES, AND OF NITRITES AND NITRATES, IN ONE OPERATION.

By CHARLOTTE F. ROBERTS.*

It has been shown† by Gooch and Gruener that nitrates may be estimated most accurately by treatment with manganese chloride, the chlorine thus liberated being collected in potassium iodide, and the amount of iodine set free determined by titration with sodium thiosulphate. In a recent paper ‡ I have shown that good results are also obtained by treatment of the nitrate with ferrous chloride, and collecting and measuring the nitric oxide evolved over sodium hydroxide with the apparatus described and pictured in that article.§

This apparatus consists essentially of a small retort fitted with a hollow, ground-glass stopper prolonged beneath in a tube, and joined above with two branching tubes through one of which carbon dioxide may enter, and the other of which is attached to a funnel-tube with stop-cock, through which liquids may be introduced without admitting air. The retort is connected with a small condenser, which in turn is attached to a Will and Varrentrapp tube containing potassium iodide, and this with a Hempel burette containing a strong solution of sodium hydroxide. In the experiments described, the potassium nitrate was introduced into the retort, carbon dioxide passed through until the air was completely driven out, and then ferrous chloride added through the funnel-tube. After heating, and passing a current of carbon dioxide through

* From Am. Jour. Sci., xlvi, 231.

† Am. Jour. Sci., xliv, 117. This volume, p. 132.

‡ Am. Jour. Sci., xlvi, 126. This volume, p. 203.

§ Fig. 8, p. 208.

the apparatus, the volume of gas unabsorbed by sodium hydroxide was measured at the observed temperature and pressure, and from this the weight of potassium nitrate was calculated. This is merely a special form of a very common method of estimating nitrates, but the apparatus is in a form which can be conveniently handled and which readily adapts itself to other uses beside the simple determination of nitrates. In a mixture of chloric and nitric acids, for example, it becomes possible by a combination of the two above-named methods for estimating nitrates, and the use of the apparatus described, to determine in one operation the amounts of each present. A method for the determination of chlorates which has long been in common use consists in treatment with hydrochloric acid, the liberated chlorine being conducted into potassium iodide, and the iodine set free determined by titration with sodium thiosulphate. This method is entirely analogous to the first mentioned method of determining nitrates, the only difference being that in the latter case a solution of manganous chloride in hydrochloric acid is used instead of the acid alone. In case of the nitrate, however, there is a second product, nitric oxide, which may be collected and measured. It would then seem possible, with the use of the apparatus heretofore described, to treat a mixture of a chlorate and nitrate with manganous chloride, pass the resulting gases through potassium iodide, and then into the Hempel burette. The amount of nitric oxide will give at once the amount of nitrate present. The iodine liberated will give the total chlorine set free by the reduction of the nitrate and chlorate. After that which is due to the nitrate determined has been deducted, we have an exact measure of the chlorate present.

To verify these presumptions, a few preliminary experiments were first made with potassium chlorate alone. In these, and all of the following experiments, great care was taken that the escaping gases should only come in contact with glass. Between the condenser and Hempel burette were two Will and Varrentrapp tubes sealed together and containing potas-

sium iodide, and generally a Geissler bulb containing potassium iodide was also added to make sure that no chlorine escaped absorption. The potassium chlorate was weighed out and introduced into the retort, air driven out by carbon dioxide, and then manganous chloride added through the funnel-tube. The liquid became dark at once, and a short heating sufficed to restore it to its original clear, light-green color. When this was accomplished, a current of carbon dioxide was passed through the apparatus, the bulbed tubes were disconnected, and their contents titrated with sodium thiosulphate. The following results were obtained from five trials:

	Wt. $KClO_3$ taken.	Wt. $KClO_3$ found.	Difference.
	grm.	grm.	grm.
(1)	0.1000	0.0990	0.0010
(2)	0.1000	0.0995	0.0005
(3)	0.0500	0.0484	0.0016
(4)	0.0500	0.0498	0.0002
(5)	0.0500	0.0496	0.0004

Working in the same way with a mixture of potassium chlorate and potassium nitrate, and estimating the amount of nitrate first from the nitric oxide produced, the following results were obtained:

		Weights taken.	Weights found.	Difference.
		grm.	grm.	grm.
(1)	Potassium chlorate	0.0500	0.0515	0.0015
	Potassium nitrate	0.0500	0.0494	0.0006
(2)	Potassium chlorate	0.0500	0.0508	0.0008
	Potassium nitrate	0.0500	0.0493	0.0007
(3)	Potassium chlorate	0.1000	0.0987	0.0013
	Potassium nitrate	0.1000	0.0995	0.0005
(4)	Potassium chlorate	0.1000	0.1007	0.0007
	Potassium nitrate	0.1000	0.0980	0.0020
(5)	Potassium chlorate	0.0300	0.0305	0.0005
	Potassium nitrate	0.1000	0.0990	0.0010
(6)	Potassium chlorate	0.1000	0.1006	0.0006
	Potassium nitrate	0.0300	0.0293	0.0007

The method is simple, rapid, and easy, and sufficiently accurate for most analytical work. One objection that may be urged against it is that any error in the determination of

the nitric acid involves a corresponding error in the amount of chloric acid, but the above results show that such errors will be quite small if the experiment is conducted with proper precautions.

It also appeared probable that a nitrate and nitrite could be estimated at one operation in a somewhat similar manner. By the action of manganous chloride on a mixture of nitric and nitrous acids, nitric oxide and iodine would be set free from each. Representing the weight of nitric oxide found by a, and the weight of iodine found by b, and letting x equal the amount of nitric acid operated upon, and y the amount of nitrous acid,

$$\frac{30}{63}x + \frac{30}{47}y = a, \text{ and}$$

$$\frac{379.5}{63}x + \frac{126.5}{47}y = b$$

whence,

$$x = 0.249\,b - 1.049\,a$$
$$y = 2.35\ \ a - 0.186\,b$$

In the attempt to verify these formulas by experiment, a little difficulty was found in getting a pure and stable nitrite upon which to operate. Some silver nitrite was prepared by precipitation from potassium nitrite and silver nitrate. This was washed well and dried as thoroughly as possible over sulphuric acid in the dark. Weighed portions were put in the retort, and after the air was expelled, manganous chloride was added. The amount of silver nitrate was then estimated from the iodine set free in the bulbed tubes, and also from the nitric oxide left in the Hempel burette. The results varied from one another by 4 or 5 per cent on different portions, but a few trials were sufficient to indicate that the trouble lay in the silver nitrite and not in the process itself. The percentage of purity as obtained from several trials by ignition was 98.4 per cent. The average of ten trials estimating from nitric oxide gave 98.1 per cent, and from the liberated iodine 98.7 per cent. This was uniformity enough to indicate that the method of work was trustworthy, although there was appar-

ently such a lack of homogeneity in the silver nitrite as to make it impossible to use it in testing the value of the formula given above.

To obviate this difficulty, more silver nitrite was precipitated, well washed, dissolved in warm water, and a solution of sodium chloride added. The silver chloride was then filtered off, and the resulting solution of sodium nitrite was used in the following experiments. To determine the strength of this solution, ten or fifteen cubic centimeters were drawn off from a burette, and the nitrite estimated with potassium permanganate according to the method of Kinnicutt and Nef.* At the same time, similar amounts were introduced into the retort with manganous chloride, and the nitrite estimated both from the liberated iodine and the nitric oxide formed. It was found that the air must be thoroughly driven out of the apparatus before the nitrite was introduced, as the carbon dioxide, passing over the solution, decomposed it with liberation of nitric oxide which, in presence of air, gave an excess of free iodine, and at the same time a little gas was lost. Accordingly, carbon dioxide was first passed through the apparatus for some time, then the nitrite was introduced through the funnel-tube and rinsed in with a little water, followed by the manganous chloride solution, care being taken that the water should not exceed one-third of the total volume of the liquid, according to the precaution shown to be necessary by Gooch and Gruener. Working in this way with the solution of sodium nitrite, the following results were obtained:

Exp.	Vol. taken.	Weight reckoned from $KMnO_4$.	Weight reckoned from NO.	Weight reckoned from iodine.
	cm.	grm.	grm.	grm.
(1)	10	0.0463	0.0456	0.0450
(2)	10	0.0460	0.0460	0.0470
(3)	15	0.0704	0.0708	0.0722
(4)	15	0.0690	0.0712	0.0750
(5)	15	0.0701	0.0704	0.0722
(6)	15	0.0688	0.0696	0.0695
(7)	15	0.0706		
(8)	15	0.0712		

* Ann. Ch. J[illegible], v, 388.

It will be seen that the results reckoned from the iodine are in general larger than those obtained by either of the other methods. This is what might be expected on account of the difficulty of completely removing air from the apparatus and solutions employed, and such air would naturally cause an excess of iodine. In (4) especially it will be noticed that we have an abnormally large amount of iodine set free, and this may undoubtedly be attributed to air, since it was observed that the current of carbon dioxide was rather sluggish at the time of that experiment.

The average of the above-recorded experiments would give as the value of fifteen cubic centimeters, from the method of Kinnicutt and Nef, 0.0697 grams, from the nitric oxide, 0.0699 grams, and from the iodine 0.0711 grams. If we assume that the mean weight per fifteen cubic centimeters is represented by the average of these three modes of determination, we obtain 0.0702 grams, and that is the number which is used in the following determinations to represent the weight of sodium nitrite in fifteen cubic centimeters of the solution. The following experiments were made in the same way as the preceding, except that potassium nitrate was introduced in the dry state before the air was driven out of the apparatus, and the results were calculated from the formula given above.

Exp.		Weights taken.	Weights found.	Difference.
		grm.	grm.	grm.
(1)	Sodium nitrite	0.0702	0.0718	0.0016
	Potassium nitrate	0.1000	0.1000	0.0000
(2)	Sodium nitrite	0.0702	0.0712	0.0010
	Potassium nitrate	0.1000	0.0999	0.0001
(3)	Sodium nitrite	0.0702	0.0710	0.0008
	Potassium nitrate	0.1000	0.1004	0.0004
(4)	Sodium nitrite	0.0702	0.0698	0.0004
	Potassium nitrate	0.1000	0.1012	0.0012
(5)	Sodium nitrite	0.0468	0.0453	0.0015
	Potassium nitrate	0.1000	0.0994	0.0006
(6)	Sodium nitrite	0.0468	0.0444	0.0024
	Potassium nitrate	0.0500	0.0513	0.0013

Though the process is one in which the most perfect accuracy cannot be assured in all cases, the above results show

that it is capable of giving fairly accurate results, sufficient for many analytical purposes. It seems to be especially well adapted to the estimation of the commercial alkali nitrites, the whole determination being made on one portion and by one operation, instead of on two different portions.

XXIX

ON THE SEPARATION OF COPPER FROM CADMIUM BY THE IODIDE METHOD.

By PHILIP E. BROWNING.*

THE separation of copper from cadmium by the precipitation of the cuprous iodide by appropriate means has long been known. Pisani† mentions the fact that potassium iodide can be used to effect precipitations and claims that a satisfactory separation can be made in this way. Flajolot‡ states that potassium iodide cannot be used as a precipitant on account of the solubility of cuprous iodide in that reagent, nor can hydriodic acid be employed if nitric acid is present. He recommends that the solution containing copper be brought to acidity with sulphuric acid, that a considerable excess of sulphurous acid be added and that the precipitation be effected by hydriodic acid. Under this treatment he finds that only an unweighable or at least a very small trace of copper remains dissolved. Kohner§ in a paper of more recent date, in which he reviews the various methods for the separation of copper from cadmium, states that the iodide method is impracticable on account of the solubility of cuprous iodide both in excess of hydriodic acid and in potassium iodide.

The work to be described was undertaken to determine if possible under what conditions the method may be safely used. Solutions of copper and cadmium sulphates were made and standardized by treating definite portions, measured from burettes and weighed, by appropriate means, the average of

* From Am. Jour. Sci., xlvi, 280.

† Compt. rend., xlvii, 294.

‡ Jour. prakt. Chem., lxi, 105.

§ Zeitschr. anal. Chem., xxvii, 203. Jour. Anal. Chem., iii, 339.

closely agreeing results being taken as the standard. A solution of potassium iodide of approximately ten per cent strength, was used throughout the work. The amount of the copper solution generally taken (25 cm^3) contained about 0.12 grm. of copper and the potassium iodide necessary to completely precipitate the iodide was about 0.6 grm. or 6 cm^3 of the solution. I have in no case used less than 10 cm^3 or 1 grm. of the iodide. In experiments (1) and (2) the free iodine separating on the addition of the potassium iodide was bleached with sulphurous acid and the cuprous iodide filtered off immediately. In experiment (3) no sulphurous acid was added but the solution was boiled until a considerable amount of the free iodine was expelled. In experiment (4) the boiling to expel the free iodine completely was necessarily carried on until the solution was evaporated nearly to dryness. Experiments (5) to (14) were made to show the effect of varying amounts of potassium iodide, and were all conducted in the same manner, the standard copper solution being measured from a burette into a counterpoised beaker and weighed, the potassium iodide in solution added, the whole evaporated to dryness to insure the expulsion of the iodine, and water added to the amount indicated in the table. The filtration was made under gentle pressure, by means of a Bunsen filtering flask on an asbestos felt contained in a perforated platinum crucible, the whole having been previously ignited and weighed. It is advisable to use a moderately thick felt and not to allow the felt to run dry nor to remove the pressure during the filtration, on account of the tendency of the cuprous iodide to pull through under these conditions. The precipitate was washed thoroughly with either hot or cold water, the washings never amounting to less than 100 cm^3. The crucible containing the cuprous iodide was placed in an air bath and the precipitate dried at a temperature between 120° C. and 150° C., and weighed. The first weight was uniformly constant. It would seem from experiments (4) to (12) that a moderate excess of potassium iodide has no great solvent effect upon the precipitated cuprous iodide, while free

iodine and large amounts of hydriodic acid have a decided solvent effect as shown in experiments (1), (2), (3). In two cases where 1 grm. and 2 grm. respectively of potassium iodide were used to precipitate about 0.12 grm. of copper the filtrate from the first gave no reaction with either ammonia or acetic acid and potassium ferrocyanide, and the second gave no reaction with ammonia and with potassium ferrocyanide only a trace.

SERIES I.*

Exp.	Copper taken.	Copper found (weighed as Cu_2I_2).	Error in copper.	KI used.	Final volume of liquid.
	grm.	grm.	grm.	grm.	cm³
(1)	0.1189	0.1093	0.0096–	1	300
(2)	0.1197	0.1050	0.0147–	1	300
(3)	0.1191	0.1056	0.0135–	1	300
(4)	0.1194	0.1189	0.0005–	1	300
(5)	0.1194	0.1196	0.0002+	1	100
(6)	0.1191	0.1194	0.0003+	1	100
(7)	0.1193	0.1193	0.0000	2	100
(8)	0.0049	0.0045	0.0004–	2	100
(9)	0.0051	0.0047	0.0004–	2	100
(10)	0.1195	0.1195	0.0000	3	100
(11)	0.1192	0.1188	0.0004–	4	100
(12)	0.1191	0.1189	0.0002–	4	200
(13)	0.1193	0.1182	0.0011–	5	200
(14)	0.1193	0.1179	0.0014–	5	200

These filtrates before testing for copper were treated with potassium nitrite and sulphuric acid to remove the iodide and oxidize the copper. I have no doubt that when the potassium iodide is in excess some copper goes into solution, but the amount is very small unless the excess of iodide is very great. I may add here that when the potassium iodide is in very large excess the mixture of potassium iodide and cuprous iodide melts as the solution becomes concentrated by evaporation and a solution is obtained having a deep iodine color. This color does not disappear on further evaporation and the result obtained upon filtering the cuprous iodide after dilution with water invariably shows considerable loss. In the event of noticing the phenomenon mentioned it is best to throw aside

* The copper is calculated as the metal in this table.

the determination before completion and start another using less of the iodide.

The separation of the copper from the cadmium was taken up next. Definite portions of the cadmium solution were measured into the same beakers with the copper solution and weighed, and enough potassium iodide was added to precipitate the whole as cuprous iodide if no cadmium were present. The solution was evaporated to dryness to remove iodine and diluted to the amount stated in the table. The precipitated cuprous iodide was filtered upon an asbestos felt, thoroughly washed, dried, and weighed as before described. The filtrate and washings contained, of course, the cadmium together with the excess of potassium iodide and potassium sulphate formed in the reaction, and the determination of the cadmium was not as simple a matter as might at first be supposed. In the presence of potassium iodide, hydrogen sulphide did not give a precipitate in acid or neutral solution which could be filtered. After removing the potassium iodide, however, by treating with sulphuric acid and potassium nitrite, it was found to be possible to precipitate all the cadmium as sulphide, but in such form that filtration was extremely slow, which was peculiarly disadvantageous in this case inasmuch as the presence of the large amount of alkaline salts present made prolonged washing of the sulphide necessary. Ammonium sulphide gave better results, the precipitate falling in good form even in the presence of potassium iodide, but here also the slow filtration was a disadvantage. I have had recourse therefore to the method of precipitating by sodium carbonate and weighing as oxide. This method has generally been regarded as inaccurate, but my experience has shown that it is one of the best of the processes employed for the estimation of cadmium when the filtrations and ignitions are made upon asbestos. Two determinations of the cadmium alone gave results agreeing closely with the standard determinations made by evaporating definite portions of the solution of the sulphate to dryness and igniting at low redness and weighing as the anhydrous sulphate.

The filtrate containing the cadmium was heated to boiling and sufficient sodium carbonate added to complete the precipitation. On further boiling the precipitate became granular and filtered easily. The precipitate was washed with hot water several times by decantation, the washings being passed through the felt to prevent loss of any of the precipitate. Washing was continued until the filtrate gave

SERIES II.

Exp.	Copper taken.	Copper found (weighed as Cu_2I_2).	Error on copper.	Cadmium taken.	Cadmium found (weighed as CdO).	Error on cadmium.	KI used.	Found volume of liquid.
	grm.	grm.	grm.	grm.	grm	grm.	grm.	cm^3
(1)	0.2383	0.2386	0.0003+	0.0484	0.0490	0.0006+	2	100
(2)	0.1192	0.1185	0.0007−	0.2439	0.2440	0.0001+	2	100
(3)	0.1193	0.1194	0.0001+	0.1942	0.1942	0.0000	2	100
(4)	0.1188	0.1190	0.0002+	0.2422	0.2421	0.0001−	2	200
(5)	0.1201	0.1201	0.0000	0.2426	0.2428	0.0002+	2	100
(6)	0.1193	0.1193	0.0000	0.2436	0.2433	0.0003−	2	100
(7)	0.0239	0.0238	0.0001−	0.1934	0.1932	0.0002−	1	100
(8)	0.0236	0.0239	0.0003+	0.1942	0.1936	0.0006−	1	100
(9)	0.0239	0.0242	0.0003+	0.1444	0.1442	0.0002−	1	100
(10)	0.0238	0.0238	0.0000	0.1467	0.1461	0.0006−	1	100

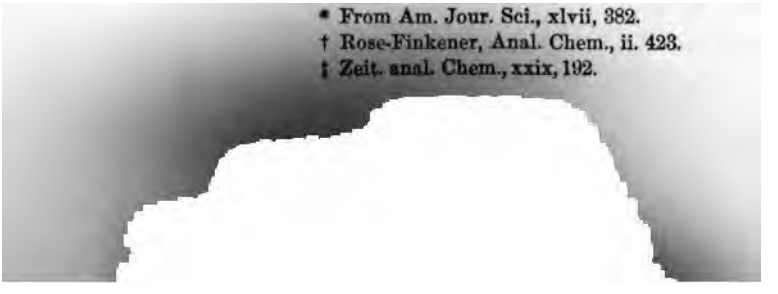
no reactions for either sulphate or iodide. The crucible containing the carbonate was heated gently at first, then gradually to a higher degree until the lower half of the crucible was red and the white carbonate had changed to the brown oxide. This heating was repeated until a constant weight was obtained. In some of the separations the faintest suspicion of a blue color in the carbonate suggested the presence of the fraction of a milligram of copper which probably escaped the separation process. The method is simple in manipulation and the results are fairly accurate.

XXX

THE DETECTION AND SEPARATION OF ARSENIC ASSOCIATED WITH ANTIMONY AND TIN.

By F. A. GOOCH and B. HODGE.*

Upon the well known fact that hot strong hydrochloric acid is capable of dissolving the sulphides of antimony and tin while exerting solvent action to a very slight degree upon arsenious sulphide is based the simplest and most rapid method in common use for the separation of arsenic from antimony and tin. Unfortunately, however, the forcible treatment necessary to bring about the solution of large amounts of antimony is sufficient† to dissolve small quantities of arsenious sulphide, so that for the purposes of general analysis the method is inadequate. Koehler‡ has shown that only the arsenic is precipitated, and that very completely, when hydrogen sulphide acts upon the solution of arsenious and antimonious salts in hydrochloric acid of 20 per cent strength, but the adaptability of Koehler's treatment to the detection of arsenic in the ordinary course of analysis is limited by the necessity of so constituting the solution to be tested that hydrogen sulphide shall occasion no deposit of free sulphur to conceal or be mistaken for a precipitation of arsenious sulphide. In the course of analysis the mixed sulphides of arsenic, antimony, and tin, remaining after the removal of the sulphides insoluble in alkaline sulphides and recovered from solution by the action of hydrochloric acid, require for their complete solution the



* From Am. Jour. Sci., xlvii, 382.
† Rose-Finkener, Anal. Chem., ii. 423.
‡ Zeit. anal. Chem., xxix, 192.

action of an oxidizing agent which must, of course, interfere with the immediate use of Koehler's method. If simple means can be found for the destruction of the excess of the oxidizing agent and the simultaneous reduction of the arsenic and antimony to the lower condition of oxidation, it is plain that the test for arsenic by passing hydrogen sulphide into the solution of antimony and tin in hot hydrochloric acid of half-strength should be sure and easy. In a former paper from this laboratory * a method was described for the quantitative separation of arsenic from antimony, based upon the reduction and volatilization of salts of arsenic by the action of a current of gaseous hydrochloric acid upon the solution containing potassium iodide. It is this reaction — the reduction of arsenic and antimony and the volatilization of the former by the simultaneous action of potassium iodide and hydrochloric acid — which we have now endeavored to apply in simple form to the rapid detection of small amounts of arsenic associated with antimony and tin. We have studied the effect of repeated distillations of small portions of concentrated hydrochloric acid upon mixtures of the salts with potassium iodide. The apparatus which we employ is essentially the distillation apparatus of Mohr, and consists of a 25 cm^3 flask fitted by means of a rubber stopper to a pipette bent, drawn out at the lower end, and dipped into a test tube which is at the same time supported and cooled in a flask partly filled with water. The pipette tube is wide enough (about 0.7 cm. in diameter) to prevent the formation of bubbles within it, and the bulb, holding about 20 cm^3, is sufficiently large to retain any liquid which may be momentarily forced back by the accidental cooling of the flask during the distillation.

In the test experiments recorded below the arsenic was introduced into the flask in the form of arsenic acid dissolved with 3 grm. of potassium iodide in 5 cm^3 of water, an equal volume of the strongest hydrochloric acid (sp. gr. 1.20) was added, the distillation was carried nearly to dryness, and the

* Gooch and Danner, Am. Jour. Sci., xlii, 308. This volume, p. 86.

distillate was condensed in 10 cm^3 of a mixture of strong hydrochloric acid and water in equal parts. The iodine evolved during the distillation was bleached by the addition to the distillate of stannous chloride dissolved in hydrochloric acid of half-strength, and hydrogen sulphide was passed to precipitate the arsenic if present. The residue in the flask was treated with 10 cm^3 of the strongest hydrochloric acid and the process of distillation was repeated, but this time the distillate was condensed in 10 cm^3 of water in order that the final acidity of the liquid should be that of acid of half-strength, and so, after bleaching by stannous chloride, immediately available for the test for arsenic by hydrogen sulphide. Subsequent treatments of the residue were carried out similarly until arsenic ceased to appear in the distillate.

The results of experiments (1) to (5) show that four successive distillations of 10 cm^3 portions of the strongest acid are enough to transfer 0.01 grm. of arsenic completely to the distillate, while a single distillation appears to be sufficient to volatilize anything less than 0.003 grm.

Experiments (6) to (9) made similarly with antimony, taken in the form of purified tartar emetic and oxidized by iodine in alkaline solution previous to treatment, either alone or with arsenic, show that antimony is discoverable in the residues when even so little as 0.0001 grm. of that element is originally introduced, though it was very evident that a portion of the antimony may pass to the distillate when much of it is present in the flask. Indeed when large quantities of antimony are treated the appearance of the brownish-red fumes of antimonious iodide in the distilling tube may serve as a very good indication that the concentration should go no further, since the antimonious iodide may, if it reaches the receiver in quantity, impart to the distillate a color which is not discharged, by the stannous chloride used to bleach the iodine and which makes it necessary to look subsequently for a precipitate of arsenious sulphide in a liquid of its own tint. The amount of antimony volatilized seems to be proportioned to the amount present, and, if the distillation is properly

conducted, enough antimony remains in the residue to be found if it was originally present in discoverable quantity.

The results of similar work with tin alone, and with tin and arsenic, are recorded in experiments (10) to (15), and the evidence goes to show that, though like antimony it may pass to the distillate under the conditions, enough tin always remains to be found in the residue, if the amount originally taken was discoverable.

Exp.	Arsenic taken as H_3O_3AsO.	Antimony taken as H_3O_3SbO.	Tin taken as $SnCl_4$.	Precipitation by H_2S in successive distillates.	Precipitation by H_2S in the residue dissolved in water.
	grm.	grm.	grm.		
(1)	0.0001	. . .	. . .	I. Found. II. None.	None.
(2)	0.0033	. . .	. . .	I. Found. II. None.	None.
(3)	0.0050	. . .	. . .	I–III. Found. IV. None.	None.
(4)	0.0100	. . .	. . .	I–IV. Found. V. None.	None.
(5)	0.1000	. . .	. . .	I–VII. Found. VIII. None.	None.
(6)	. . .	0.0001	. . .	I. None.	Distinct color.
(7)	0.0050	0.0001	. . .	I–IV. Found. V. None.	Distinct color.
(8)	0.0001	0.4	. . .	I. Found. II. None.	Large.
(9)	0.0100	0.4	. . .	I–IV. Found. V. None.	Large.
(10)	. . .	. . .	0.0001	I. None.	Distinct color.
(11)	0.0100	. . .	0.0001	I–IV. Found. V. None.	Distinct color.
(12)	0.0001	. . .	0.0005	I. Found. II. None.	Distinct.
(13)	0.0100	. . .	0.0005	I–IV. Found. V. None.	Distinct.
(14)	0.0001	. . .	0.5	I. Found. II. None.	Large.
(15)	0.0100	. . .	0.5	I–IV. Found. V. None.	Large.

It is plain that a single distillation, which may easily be completed in five minutes, is sufficient to discover the presence of 0.0001 grm. of arsenic associated with so much as 0.4 grm. or 0.5 grm. of antimony or tin.

It is also evident that amounts of arsenic not exceeding 0.003 grm. may be completely removed from the residue by

a single distillation. When larger amounts of arsenic are to be removed, so that the tin and antimony may be obtained free from that element, the result may be accomplished by repeating the distillation sufficiently; or, inasmuch as only a little iodine remains after the first distillation, the end may be attained by dissolving the residue in hydrochloric acid of half-strength, bleaching the iodine with exactly the necessary amount of sulphurous acid or sodium thiosulphate (since the use of the stannous chloride is here precluded), and passing hydrogen sulphide.

XXXI

ON THE BLUE IODIDE OF STARCH.

By CHARLOTTE F. ROBERTS.*

The interesting article by Mylius† on the composition of blue iodide of starch, and the reply to the same by Stocks,‡ have suggested to me a few simple experiments, the record of which will perhaps be interesting to others who, like myself, may have been puzzled to decide between the adverse views, especially since the papers above referred to are somewhat lacking, in certain portions, in experimental evidence of the facts stated.

Mylius derives as the formula for the blue iodide of starch $(C_6H_{10}O_5I)_nHI$, in which n probably equals 4, and states that it is formed by the union of the colorless, or yellow, compound $C_6H_{10}O_5I$ with hydriodic acid or one of its salts. He affirms that a pure solution of iodine and starch gives no blue color, but that the liquid must contain an iodide, a trace of which is sufficient to bring about the desired result.

My own study of the blue iodide of starch may be considered under two heads:

1st. Its Decompositions.

2d. The Conditions of its Formation.

1. *Decomposition of Starch Blue.*

(*a*) By heat. The effect of heat on the blue iodide of starch is well known. If moderately heated, the blue color returns on cooling, but if strongly heated, in an open vessel, it

* From Am. Jour. Sci., xlvii, 422.

† Ber. Dtsch. chem. Ges., xx, 688.

‡ Chem. News, lvi, 212.

remains permanently colorless. The explanations of this change, however, have been varied, some authorities stating that all of the iodine is driven off by the stronger heat, others that it is converted into iodic acid, and still others that the product of the reaction is hydriodic acid. Stocks affirms the last, and a very simple experiment seems to support this view. If to the cooled, colorless liquid, a few drops of iodic acid be added, the clear blue color is immediately restored. This experiment was performed in a platinum vessel, and the same results were obtained whether iodic acid were used alone or mixed with dilute sulphuric acid, though the latter acid by itself has no effect in restoring the color. That unaltered starch remains in this solution after heating, is proved by the fact that a drop of iodine colors the cold solution blue.

While the fact that hydriodic acid is split off from the iodide of starch under the influence of heat cannot be used as an argument either for or against Mylius's views, these phenomena are perhaps what might be expected if his views be correct. The first effect of heat seems to be to produce a kind of dissociation, the hydriodic acid splitting off from the rest of the molecule and going back into it when cooled, but upon longer heating the iodine which is directly united with the starch molecule is either driven from the liquid or converted into hydriodic acid. Upon the addition of iodic acid, some iodine is set free which, along with the hydriodic acid, unites with the starch to form the blue color. These phenomena are thus shown to be in harmony with Mylius's theory, although no proof of its correctness.

(*b*) By iodic acid. If some blue iodide of starch be precipitated and well washed with dilute sulphuric acid, and then iodic acid added, the solid dissolves to an apparently colorless liquid. That this solution, however, contains free iodine, may be proved by adding chloroform, which becomes tinged a decided pink. This would indicate that the iodic acid acted by withdrawing hydriodic acid from the molecule, thus setting free iodine.

(*c*) By a solution of a silver salt. One of the strongest

proofs which Mylius gives for the correctness of his views is that the blue color is destroyed by a silver salt, that the addition of pure iodine now does not restore the color, only turning it yellow, but that the addition of hydriodic acid or potassium iodide gives the blue at once.

I have found, in fact, that a single drop of a very dilute solution of silver nitrate is sufficient to destroy the deep blue color in a test-tube full of liquid. A natural explanation, in the light of the preceding experiments, is that the silver nitrate withdraws hydriodic acid; and the ease and completeness of the change supports the view that this exists as such in the molecule, since in many organic compounds, the halogen is extracted only with difficulty if at all by silver nitrate. This view is still further supported by the fact that the blue color is immediately restored by the addition of a little hydriodic acid. The color is also restored, though not to its former depth, by the addition of a few drops of strong hydrochloric acid, or by a larger quantity of the dilute acid, though it is not affected by sulphuric acid. This can readily be explained on the supposition that the silver iodide is partially decomposed by the hydrochloric acid, giving sufficient hydriodic acid to form some of the blue iodide. That this is the correct explanation rather than that hydrochloric acid can be substituted for hydriodic in the starch compound without changing its color is proved by filtering after adding silver nitrate, and adding hydrochloric acid to the filtrate, when no blue color is produced.

If we concede that in all three of these cases the decomposition has been effected by a withdrawal of hydriodic acid, it certainly shows a tendency for that portion of the molecule to split off, which is suggestive of its existing already formed as such in the molecule, and in so far is in harmony with Mylius's views, though the mere fact that hydriodic acid is withdrawn is no proof that it goes into the molecule as such. The only portion of the above which can be considered at all as direct proof of Mylius's statement is that after the blue color has been destroyed by silver nitrate, it can be reformed

by the addition of hydriodic acid. This would seem certainly a strong argument in support of Mylius.

We pass next to the consideration of

2. *The Conditions of Formation of Blue Iodide of Starch.*

Mylius makes three statements in regard to this which may be quoted here.

(1) An aqueous solution of iodine cannot color starch blue, but the color appears immediately if a trace of hydriodic acid or potassium iodide be added.

(2) Iodine solutions which color starch blue contain hydriodic acid or one of its salts.

(3) The presence of substances which destroy hydriodic acid, as, for example, chlorine and iodic acid, prevents the formation of starch blue.

These different statements will be considered in the order in which they are here quoted, but (1) and (2) are so nearly identical that they cannot be kept separate.

I have never succeeded in obtaining aqueous solutions of iodine and starch which, upon being mixed, did not produce a blue color, although great care was taken to avoid the possibility of any alkali from glass getting into the solutions. According to Mylius, this is the great cause of the presence of iodide in an iodine solution. In my experiments, the iodine was powdered, left standing for some time in a mixture of iodic and sulphuric acids, then washed thoroughly with water, and finally dissolved in water, all of these processes being carried on in a platinum dish. An emulsion of arrow-root, also well washed, was made in a platinum dish, and the two solutions were mixed in a platinum crucible. Notwithstanding all of these precautions, the blue color appeared immediately. This would seem to indicate that Mylius's views were erroneous, but on the other hand, I was able to prove the presence of hydriodic acid in my aqueous solution, even thus c: :fully prepared. I did this by shaking the solution th chloroform and separating the two liquids with se ing funnel, and repeated this

until the chloroform added remained perfectly colorless. Then, upon the addition of a few drops of iodic acid, and shaking, the chloroform became faintly but undoubtedly tinged with pink. It is proved, then, that this liquid which colored starch contained hydriodic acid, but it still remains an open question whether this iodide was an impurity in the iodine, not removed by its repeated washings, which seems hardly probable, or whether it is formed whenever iodine dissolves in water, and is therefore, in traces, a necessary accompaniment of every iodine solution.

That glass has more powerful action on an iodine solution than has generally been supposed cannot however be doubted. My own attention has been drawn to this fact by the difference in behavior of the liquid which results when starch blue is heated in a glass tube and that which is formed when the same compound is heated in a platinum vessel. In the first case the cold, colorless solution is turned blue by the addition of any acid, whereas in the latter case, iodic acid is the only one which has this power. In case sulphuric acid is added to the liquid before heating in the test-tube, the color is not restored by any acid, even iodic.

Although I have found it impossible to mix carefully prepared solutions of iodine and starch without getting a blue color, if only a drop or two of iodine be added to an excess of starch, the blue formed where the liquids first touch disappears in the mass of the liquid, and then the addition of hydriodic acid brings out the blue color distinctly. This is in harmony with Mylius's statements, and also with the fact that in working with dilute solutions in a large bulk of alkaline liquid the delicacy of the starch test for iodine is increased by the addition of two or three grams of potassium iodide.

In a further effort to prepare iodine free from iodides, I have taken an iodine solution, shaken it with chloroform, rinsed with water, and finally drawn off the chloroform solution. Then, upon adding pure water and shaking some of the mixture with starch, the starch remains uncolored. If,

however, this mixture of iodine in chloroform and pure water be heated and then cooled, or if it be exposed to the sunlight in a platinum dish for about an hour, the mixture acquires the power of coloring starch immediately, and the colorless aqueous portion of yielding iodine to chloroform when treated with iodic acid. The appearance of free iodine, indicated by the chloroform, showed that hydriodic acid had been formed by the iodine and water on heating or in sunlight.

It has just been shown that if a solution of iodine in chloroform be washed with water, separated from the aqueous portion, and starch added, there is no immediate change of color; but the blue color may be brought out in three different ways:

(1) By addition of a drop of dilute hydriodic acid.

(2) By heating and then cooling the liquid.

(3) By long standing.

The evidence of (1) is a direct support of Mylius's views, and (2) and (3) may be considered as indirectly indicative of the same, since they give conditions under which hydriodic acid might presumably be developed. Further evidence in the same direction may be found in the following experiment. An emulsion of starch in chloroform was made, and to this a solution of iodine in chloroform added. The color remained unaltered, but the addition of a little potassium iodide, either in the solid form or in aqueous solution, immediately produced the blue color. The addition of pure water failed to give the blue color until after standing for several hours.

There seems, then, to be sufficient evidence that all solutions which form starch blue contain an iodide, and also, considering the experiments with chloroform, that solutions freed from hydriodic acid cannot produce that color, although in my experiments I have not been able to make an *aqueous* solution of iodine which did not turn starch blue, and which did not contain hydriodic acid.

We pass now to the third argument of Mylius quoted above, viz.: the deterrent action of chlorine and iodic acid on the formation of starch blue.

In regard to the action of chlorine, Stocks quotes the suggestion of Miller that it may be due to the formation of iodine chloride, which is well known to have a destructive effect on the blue iodide of starch. But even granting this as an explanation, two questions remain to be answered; first, how is the iodine chloride formed, and second, what is its action on starch blue? It can hardly be supposed that the chlorine withdraws the iodine bodily from the organic molecule. A much more natural assumption would be that the chlorine decomposes hydriodic acid, setting free iodine; and here we have sufficient cause for the destruction of the blue color. But granting that the reaction may go farther, and the iodine thus set free unite with an excess of chlorine to form iodine chloride, is not this also a body which might be expected to act by destroying hydriodic acid? I have found, in fact, that when iodine chloride is added to starch blue, iodine is set free, the result which might be expected if the iodine chloride acts upon the hydriodic acid in the compound according to the reaction:

$$HI + ICl = HCl + I_2$$

This experiment was performed as follows: Iodine chloride was prepared by putting together potassium iodide and hydrochloric acid in an excess of iodic acid. It was then separated from the other bodies by extraction with ether, and to the ethereal solution starch blue was added. The color was taken from the starch, and the ether became darker and brown. To prove that this change in the ether was really due to free iodine, it was left standing over pure water for some time, with occasional shaking. Finally, some of this aqueous portion was shaken with chloroform, to which it gave the characteristic pinkish tinge. As iodine chloride gives no color to chloroform, this shows conclusively that iodine had been set free.

There remains to be considered only the action of iodic acid on the iodide of starch. Its action on the precipitated blue after formation has already been referred to, so that, at this point, we need only consider its action in preventing the formation of starch blue.

It is an undeniable fact that when dilute solutions of iodine are used, iodic acid in sufficiently large quantities prevents the formation of starch blue both when used alone, and when used with other acids, but a much smaller amount of iodic acid is necessary if mixed with another acid, as for example, sulphuric acid. This may be explained either on the assumption of a more rapid action when sulphuric acid is used, as Landolt * has found to be the case in the reaction between iodic acid and sulphurous oxide, or in the case of ordinary iodine solutions prepared and kept in glass vessels, it may be supposed due to the fact that the liquid contains iodides and iodates derived from the glass. I have tried bringing together extremely dilute solutions of iodic acid and of potassium iodide, and found that no perceptible amount of iodine is set free, though in more concentrated solutions the iodine is set free in nearly the quantitative yield represented by the equation:

$$5KI + 6HIO_3 = 5KIO_3 + 3H_2O + 3I_2$$

In this reaction, however, the amount of iodine found is always a trifle too low, probably due to the fact above shown, viz: that in very dilute solutions, the iodide and iodic acid do not react on each other, except in presence of another acid. The dilute sulphuric acid alone when added to starch blue does not bleach the color, but diminishes the intensity to an appreciable degree.

The amount of iodic acid necessary to prevent the formation of the blue color depends not only on the amount of other acid present but also on the order in which the reagents are put together. Thus I have found in several cases that, with a definite amount of iodic acid and iodine, there was no color produced if the iodine, iodic acid, and sulphuric acid were mixed first, and left standing for some minutes or half an hour before adding the starch; whereas, if the starch were put in first and the other three constituents added directly, a blue color would result which could only be destroyed on long standing and shaking, if at all.

* [illegible] Chem., xx, 745.

In general, the amount of iodic acid necessary to prevent the formation of the starch blue seems in very great excess of that which would be necessary to destroy all of the hydriodic acid which can possibly be present. It is only by following the precautions suggested above that the iodic acid needed can be made to bear any reasonable relation to this hydriodic acid. I have dissolved iodine in a mixture of iodic and sulphuric acids, and added starch and obtained immediately a blue color, though naturally not as deep and intense as would be obtained without the iodic acid. This solution was as strong as possible of iodine, being made up with powdered iodine in a platinum dish, and containing always some of the undissolved solid. The liquid poured off from this, whether filtered or not, and even when it had considerable iodic acid added to it, refused under any circumstances to give a colorless liquid with starch; and the same was found true even when it was left standing with additional iodic acid for half an hour before the starch was added.

These facts, and the fact that the purest possible freshly prepared aqueous solution of iodine may be shown to contain hydriodic acid, have suggested to me the possibility that hydriodic acid may be constantly forming in traces when iodine dissolves in water, and that, therefore, no aqueous solution can be free from it whether kept in glass or not, though there is no doubt that the glass may greatly increase the amount. So many facts seem to point to the truth that hydriodic acid or one of its salts is taken up as such into the molecule of the blue iodide of starch that the fact of the large amount of iodic acid necessary to prevent its formation can hardly be considered a sufficient argument against that belief, though we naturally question what may be the reason for this necessary excess. There seem to me to be two possible explanations, either the iodic acid destroys hydriodic acid much less readily in dilute solutions than has been generally supposed, or some hydriodic acid is constantly being formed in an iodine solution, and perhaps the correct explanation lies in the union of these two.

Landolt* has made some investigation of the reaction between iodic acid and hydriodic acid in dilute solutions, and has found that in an extremely dilute solution, nineteen seconds may elapse before the formation of iodine makes itself manifest by the blue color given to starch. I have used even diluter solutions than he, and found that with 0.000009 grams iodic acid and 0.000033 grams potassium iodide in 20 cubic centimeters of water, no color appeared with starch until several minutes had elapsed if only a small quantity of sulphuric acid was present, whereas if one-fourth of the liquid consisted of dilute sulphuric acid, a blue tinge appeared immediately. The completeness of the reaction in a given time, then, is seen to depend on the amount of sulphuric acid present, and there is nothing to show whether it is finally complete or whether there may be left traces of undecomposed hydriodic acid.

If we assume that hydriodic acid is constantly being formed in traces in an iodine solution, and remember that the reaction between hydriodic acid and iodic acid is not an immediate one in the presence of a large quantity of water, we can understand why a considerable excess of iodic acid must be used in order to destroy completely the last traces of hydriodic acid and thus entirely prevent the formation of starch blue.

*Ber. Dtsch. chem. Ges., xix, 1317.

XXXII

THE DETECTION OF ALKALINE PERCHLORATES ASSOCIATED WITH CHLORIDES, CHLORATES, AND NITRATES.

By F. A. GOOCH and D. ALBERT KREIDER.*

THOUGH perchloric acid in the free state is an exceedingly active body, its combinations with alkaline metals are, as is well known, so characterized by inertness toward ordinary reagents that in order to effect its detection it has been customary to place dependence either upon the insolubility of the potassium salt in alcohol, or upon tests for the corresponding chloride derived by ignition.

In experimenting at high temperatures upon mixtures of potassium perchlorate with salts of the halogens we have found it possible to effect the liberation of the halogen to a greater or less degree by the oxygen of the perchlorate, but the amount thus evolved has never been sufficiently complete or regular to warrant the application of the reaction to the quantitative determination of the perchlorate. In two parallel experiments, for example, a mixture of the double chloride of aluminum and sodium with 0.05 grm. of potassium perchlorate evolved in fusion in a tubulated flask (which was fitted by a ground joint to an inlet tube carrying a constant current of carbon dioxide and connected with Will and Varrentrapp absorption bulbs filled with a solution of potassium iodide), an amount of chlorine corresponding to 0.0482 grm., and 0.0460 grm. of the perchlorate. A similar experiment conducted in an atmosphere of hydrochloric acid gas and carbon dioxide in mixture yielded chlorine amounting to 0.0477 grm. of the perchlorate. Fusion of the perchlorate

* From Am. Jour. Sci., xlviii.

with cadmium iodide resulted in the liberation of much oxygen accompanying the iodine, and a mixture of zinc chloride with potassium iodide (melting at about 200° C.), yielded a large evolution of oxygen which was somewhat diminished but not wholly prevented when manganese chloride was included in the mixture. A series of fourteen experiments in which mixtures of the perchlorate with potassium iodide were treated with meta-phosphoric acid (made by heating the syrupy ortho-acid to 360° C.) in an atmosphere of carbon dioxide showed deficits in the amounts of iodine evolved amounting to 1.7 per cent, on the average, between extremes of 3.6 per cent in excess and 7.7 per cent in deficiency, and these particular experiments doubtless point to a more complete utilization of the oxygen of the perchlorate than was actually attained owing to the inevitable partial decomposition of hydriodic acid at the temperature necessary to effect the decomposition of the perchlorate.

We have, however, succeeded in developing a simple and delicate method of detecting perchlorates, and one which may be applied without great sacrifice of delicacy to mixtures of the perchlorates with chlorides, chlorates, and nitrates. It is evident that for a rapid qualitative test conditions should be so chosen that the effect of atmospheric air shall not interfere with the certainty of the indication. Of the various salts which we have employed we choose by preference fused zinc chloride, chiefly because, while sufficiently energetic in its action upon the perchlorate, it does not, like manganese chloride or the double chloride of aluminum and sodium, evolve chlorine under the influence of ordinary air at the high temperature of the reaction.

In the experiments recorded in Table I. portions of a solution of potassium perchlorate were evaporated to dryness in a test tube and the residue was fused with anhydrous zinc chloride. A trap made by cutting off an ordinary two-bulbed straight drying tube was hung with the larger end downward in the test tube, after moistening the interior of the bulbs with a solution of potassium iodide. The chlorine evolved

during the heating was registered by the iodine set free from the iodide and subsequently washed with a little water from the trap and tested with starch emulsion.

TABLE I.

$KClO_4$ taken.	Indication by the starch test.
grm.	
0.00100	Strong.
0.00050	Strong.
0.00020	Strong.
0.00010	Strong.
0.00010	Strong.
0.00005	Distinct.
0.00005	Distinct.
0.00003	Trace.
0.00003	None.
0.00001	None.
0.00000	None.

The test for 0.00005 grm. of potassium perchlorate is sure and distinct; and it is, of course, evident that the presence of a chloride in the original test can in no way interfere with the certainty of the indication. All substances, however, which yield chlorine by decomposition or by the action of the air must be removed or destroyed before the application of the test. We find by experiment that 0.1 grm. of potassium chlorate is completely broken up by treatment with 5 cm^3 of the strongest hydrochloric acid and evaporation to dryness. Nitric acid does not yield so readily to the decomposing action of hydrochloric acid and may be detected in the residue after four similar treatments. To destroy nitrates, therefore, we followed the general plan of decomposition employed in a quantitative method for the determination of nitrates previously elaborated in this laboratory * and treated the dry substance to be tested with 2 cm^3 of a saturated solution of manganous chloride in the strongest hydrochloric acid. The liquid was evaporated to dryness, and the residue was again treated similarly with one or two cubic centimeters of strong hydrochloric acid. This method of decomposing

* Gooch and Gruener, Am. Jour. Sci., xliv, 117. This volume, p. 132.

the nitrate is peculiarly advantageous since the decomposing agent is itself an excellent indicator of the completeness of the work of removal. Two or three treatments serve to remove the nitrate entirely; but before proceeding with the test it is necessary to remove the manganese which has been introduced, inasmuch as manganese chloride will of itself evolve chlorine, by exchange for oxygen, when heated in air. Sodium carbonate in solution answers the purpose of removing the manganese (together with other interfering substances) and the filtrate from the precipitated manganous carbonate leaves on evaporation a residue, which, when treated with the anhydrous zinc chloride, gives indications for the perchlorate if it is present in appreciable amount. The results of a series of tests for potassium perchlorate associated with the chlorate and nitrate of the same element are recorded in the following table.

TABLE II.

$KClO_4$ taken.	$KClO_3$ taken.	KNO_3 taken.	Treatment for the removal of chlorate and nitrate.	Indication of the perchlorate.
grm.	grm.	grm.		
0.0005	. .	. .	By HCl	Strong.
0.0003	. .	. .	By HCl	Strong.
0.0002	. .	. .	By HCl	Good.
0.0001	. .	. .	By HCl	Good.
0.0001	. .	. .	By HCl	Trace.
0.0005	0.1	0.1	By HCl + $MnCl_2$	Strong.
0.0003	0.1	0.1	By HCl + $MnCl_2$	Good.
0.0003	0.1	0.1	By HCl + $MnCl_2$	Good.
0.0002	0.1	0.1	By HCl + $MnCl_2$	Trace.
0.0001	0.1	0.1	By HCl + $MnCl_2$	Trace.
0.0000	0.1	0.1	By HCl + $MnCl_2$	None.

It is plain that 0.0001 grm. of potassium perchlorate may be found with certainty when associated with 0.1 grm. of the nitrate or chlorate or both.

XXXIII

THE ACTION OF REDUCING AGENTS ON IODIC ACID.

By CHARLOTTE F. ROBERTS.*

I. *The Absorption of Nitric Oxide by Iodic Acid.*

THE following investigations were first undertaken with the object of studying the solubility of nitric oxide in iodic acid. Although most chemical authorities agree in the statement that nitric oxide is absorbed by iodic acid with the separation of iodine, there is a certain indefiniteness with regard to the degree of solubility, which led me to investigate the subject for myself. Thus, Gmelin-Kraut states that "All the lower oxides of nitrogen decompose iodic acid into iodine and nitric acid, but the decomposition takes place only in presence of a considerable quantity of water," but the degree of ease with which the decomposition takes place meets with no comment, and the "considerable quantity of water" seems a somewhat indefinite condition. Kammerer,† who is the authority referred to for the above facts, and who, some years ago, made a thorough study of iodic acid, says, without referring to any illustrative experiments, "At ordinary temperature, I_2O_5 is reduced only in aqueous solution by nitric oxide, but this gas is without action upon the water-free acid and its solution in concentrated sulphuric acid. At 100° the latter is very slowly, the water-free acid not at all decomposed."

A portion of this latter statement was very easily verified. Some nitric oxide was passed through the dry acid, and other portions were collected and allowed to stand over sulphuric acid solutions of HIO_3 and I_2O_5, without any appreciable separation of iodine.

* From Am. Jour. Sci., xlviii, 151. † Jour. prak. Chem., lxxxiii, 73.

In order to test the solubility of the gas in aqueous solutions of iodic acid, the nitric oxide was prepared in a generator containing potassium nitrate and ferrous sulphate, the air having been previously driven from the apparatus by means of carbon dioxide. The gas was next passed into a Will and Varrentrapp tube containing potassium iodide, and then into a Geissler bulb containing the iodic acid. The experiment was made several times with iodic acid of various degrees of concentration, and always with the same result. There was no evidence of iodine being set free from the iodic acid, though the liquid showed occasionally a barely perceptible tinge of yellow. There was, however, a smaller amount of nitric oxide collected, by two or three cubic centimeters, than should have resulted from the amount of nitrate used, and, on two or three occasions, an odor like that of chlorine was observed about the Geissler bulb when the apparatus was disconnected, which could only be explained on the supposition that gaseous hydrochloric acid was carried over from the generator through the potassium iodide.

A later experiment in which nitric oxide was collected in a tube containing iodic acid and hydrochloric acid so dilute that no reaction took place between the two acids in the cold, showed that under these circumstances the nitric oxide was absorbed without any separation of iodine and that the liquid became yellow and gave an odor like that of chlorine, so that the above seemed a plausible explanation of the disappearance of some nitric oxide in the Geissler bulb without a simultaneous liberation of iodine.

Two or three experiments were then made with the apparatus as before excepting the addition of a new absorption tube containing silver nitrate to prevent the hydrochloric acid from going over into the iodic acid. Still there was no evidence of iodine being set free. It seemed apparent, then, that the nitric oxide was not so soluble in iodic acid that it could be absorbed by simply passing it rapidly through the solution.

To determine whether the gas was soluble upon long

contact with the iodic acid or not, different portions were collected in U tubes closed at one end and filled with solutions of iodic acid of different degrees of concentration. The gas had been collected and allowed to stand over potassium iodide and sodium hydroxide for from twenty-four to forty-eight hours before being transferred to the U tube, in order to remove completely any other oxide of nitrogen which might be present. Solutions of iodic acid were used in the different U tubes varying from a saturated solution containing about 50 grams to 25 cubic centimeters to a rather dilute solution containing not more than 5 grams to 25 cubic centimeters. There was no apparent absorption as the gas passed up through the liquid, but after the nitric oxide had been standing over the iodic acid for a few moments, iodine appeared on the surface of the liquid. This deposit gradually increased in amount and the liquid rose in the tube, reaching its maximum in twenty-four hours or less, depending on the amount of gas used.

The result of my experiments, then, has been to show that nitric oxide is absorbed by solutions of iodic acid of any degree of strength, but the reaction takes place slowly even when the gas is confined over the acid, and not at all when passed rapidly through the solution.

II. *The Action of Reducing Agents on Iodic Acid in the presence of Hydrochloric Acid.*

It has already been stated that when the nitric oxide was collected over iodic acid mixed with dilute hydrochloric acid the gas was absorbed, but there was no liberation of iodine, and in some cases an odor like that of chlorine was observed when the tube was opened. A similar phenomenon was noticed with several other reducing agents. It is well known that iodic acid with strong hydrochloric acid, or heated with dilute hydrochloric acid, forms iodine chloride and may set free chlorine, but in these experiments the dilute acids were used in the cold, and there was no change apparent until the reducing agent was added. Besides the nitric oxide,

other substances which had a similar effect were potassium iodide, sodium thiosulphate, arsenious oxide, ferrous sulphate, stannous chloride, and potassium sulphocyanide. If the reducing agent was added in a very concentrated form, iodine was sometimes evolved, and in many cases traces of iodine would first form where the reagent touched the liquid, but would disappear on shaking, and a light yellow liquid would result with an odor like that of chlorine.

The first explanation of this phenomenon that suggested itself was that the iodic acid was not immediately completely deoxidized by the reducing agent but was first transformed to a lower oxide of iodine* which was more active and therefore more easily acted upon by hydrochloric acid than the iodic acid itself, and that the chlorine thus set free united wholly or partially with the iodine formed by the first reduction. It was with the object of studying the reduction of iodic acid in the presence of hydrochloric acid that some experiments were undertaken with potassium iodide, iodic acid, and dilute hydrochloric acid. Potassium iodide was chosen as the reducing agent on account of the simplicity of its oxidation products. Approximately $\frac{N}{10}$ solutions of iodic acid and potassium iodide were used and dilute hydrochloric acid of specific gravity 1.05. The latter acid was so dilute that it could be added in apparently indefinite quantities to the iodic acid without producing any perceptible odor or change of color.

With 10 cm^3 of iodic acid and half that volume of hydrochloric acid, if the potassium iodide was added gradually from a burette, the addition of 4 or 5 cubic centimeters gave a clear light yellow liquid in which no free iodine could be proved either by starch or chloroform. As the amount of potassium iodide increases, the liquid gradually becomes orange until finally particles of iodine are precipitated out and accumulate until they reach the quantitative yield represented by the common equation:

$$5KI + HIO_3 + 5HCl = 3H_2O + 5KCl + 3I_2$$

* Gmelin-Kraut, Anorganische Chemie, I, 2.

These phenomena seem to indicate that the reaction takes place in two steps, giving first the iodine chloride, and then the decomposition of this by means of more potassium iodide setting free iodine. Even after solid particles of iodine appear in the liquid, starch paste is not colored blue, showing the well-known disturbing action of the chloride of iodine. That the intermediate product is essentially the monochloride of iodine instead of the trichloride may be inferred from the superior stability of the former in dilute solutions containing hydrochloric acid, since most authorities agree that the trichloride is completely broken up in dilute solutions into the monochloride, iodic acid and hydrochloric acid. If any trichloride were first formed and underwent this decomposition, the final form of the reaction would be the same as if the monochloride were the sole product. This inference was further confirmed by later results and by the following experiment.

The clear yellow liquid obtained by putting together 10 cubic centimeters of iodic acid, half that volume of hydrochloric acid, and 4 cubic centimeters of potassium iodide was agitated with benzene which is said to dissolve iodine trichloride with a dark cherry-red color.* The result was a barely perceptible pinkish tinge to the benzene, which left no appreciable residue on evaporation. After separating the benzene and adding ether, the color was quickly taken from the aqueous solution, and the ether became yellow and, on evaporation, left a considerable quantity of a volatile reddish-brown liquid. This experiment showed plainly that the essential product was iodine monochloride.

In three different ways I have tried to estimate the proportions in which iodic acid and potassium iodide unite in presence of an excess of the former and hydrochloric acid. The direct method of letting potassium iodide of known strength slowly into a mixture of the two acids and determining the first appearance of free iodine is difficult on account of the action of the iodine chloride on the blue iodide of starch which

* Ladenburg, Handwörterbuch, v, 359.

one would naturally use as an indicator. I have succeeded, however, in getting an approximate result, by taking out a drop of the liquid from time to time and testing on starch paper. With 5 cubic centimeters of iodic acid, 9.5 cubic centimeters of potassium iodide were added before there was any effect on the starch paper. This would indicate molecular proportions of iodic acid to potassium iodide as 1 : 1.9.

In the second method, 20 cubic centimeters of iodic acid, 10 of hydrochloric acid, and 4 of potassium iodide were put together, the resulting iodine chloride was extracted with ether and separated with a separating funnel. The aqueous solution containing free hydrochloric acid was then treated with an excess of potassium iodide and the amount of iodine set free determined, after neutralization, by alkaline arsenious acid. From this the iodic acid remaining in the solution after the extraction of the iodine chloride could be readily estimated, and the difference between this and the amount taken gave the amount used in the reaction. Three trials of this experiment gave the following results for the molecular proportions in which the iodic acid and potassium iodide unite in presence of hydrochloric acid while the iodic acid is in excess:

$$\left.\begin{array}{l} HIO_3 : KI \\ 1 : 2.06 \\ 1 : 1.99 \\ 1 : 1.9 \end{array}\right\} \text{Average} = 1 : 1.98.$$

The third method consisted in putting together the reagents in the same proportions as above and then decomposing the iodine chloride with acid potassium carbonate and estimating by alkaline arsenious acid the iodine set free. According to Gay-Lussac, the reaction between iodine chloride and an alkali is represented thus:

$$6KOH + 5ICl = 5KCl + KIO_3 + 3H_2O + 2I_2.$$

The iodine shown by the arsenious acid is then only $\frac{4}{5}$ of that in the iodine chloride. Making this correction and knowing the amount of iodine in the potassium iodide used, it becomes

an easy matter to determine the iodic acid which has contributed to the formation of the iodine chloride.

The following results were obtained:

$$\left.\begin{array}{l} HIO_3 : KI \\ 1 : 1.92 \\ 1 : 2.02 \end{array}\right\} \text{Average} = 1 : 1.97.$$

The three methods, then, agree fairly well in indicating two molecules of potassium iodide to one of iodic acid, a reaction which would be expressed by the following equation:

$$HIO_3 + 2KI + 5HCl = 3H_2O + 2KCl + 3ICl.$$

The formation of iodine monochloride has thus been proved by three methods, two of which would be sufficient to establish the reaction. The first two methods are independent of the reaction between iodine monochloride and carbonated alkalies, while the third depends directly upon that reaction. Assuming the correctness of Gay-Lussac's equation, this third method may be taken simply as an additional way of proving what has been already sufficiently established in two different ways. On the other hand, considering the formation of iodine chloride sufficiently established by the two other methods, the last set of experiments may be used to discriminate between Gay-Lussac's and Grüneberg's reactions. The latter * states, without describing his work in detail, that he has found by many carefully repeated experiments that the action of alkaline carbonates on iodine monochloride gives potassium chloride and potassium chlorate and all of the iodine is set free. My results, however, show the correctness of Gay-Lussac's equation, since it is only on the assumption that four-fifths of the iodine is set free that my third method of work gives results corresponding with those obtained in two other ways. Moreover, some iodine chloride was prepared by putting together potassium iodide, and an excess of iodic and hydrochloric acids, and extracting with ether, specially purified by standing over sodium bisulphite and distilling from sodium hydroxide. Portions of this ethereal solution were drawn off from a burette and treated with potas-

* Jour. prakt. Chem., lx, 172.

sium iodide, and the iodine estimated by sodium thiosulphate. Similar portions were then treated with hydrogen potassium carbonate, and the iodine estimated by arsenious acid. Grüneberg's reaction would demand that one-half as much iodine should be set free in the latter case as in the former, instead of which only four-fifths of that amount was found, which is in direct agreement with Gay-Lussac's equation.

III. *Action of Iodine on Iodic Acid in presence of Hydrochloric Acid.*

Some light is thrown upon the reaction just established by the behavior of free iodine in a mixture of iodic and hydrochloric acids.

Although a solution of iodine in iodic acid turns starch blue, and also one of iodine in hydrochloric acid, if the solutions be mixed the starch immediately loses its color, but regains it on the addition of alkaline carbonate. Also, if a colorless mixture of iodic and hydrochloric acids be taken, and aqueous iodine added gradually from a burette, the first effect of the addition is to make a colorless liquid in which the presence of iodine can be proved only upon addition of an alkaline carbonate. Further addition of the iodine gives a yellow liquid whose properties and reactions seem identical with that obtained by putting together iodic and hydrochloric acids and potassium iodide. This same liquid may be produced by allowing iodine to dissolve slowly in the cold in a mixture of dilute hydrochloric and iodic acids.

Apparently, then, the action of reducing agents is to set free iodine from the iodic acid, and this dissolves in a mixture of iodic and hydrochloric acids to form iodine chloride. Two experiments were made to determine the proportions in which the iodine and iodic acid unite in this reaction. Solid iodine, in carefully weighed quantity, was allowed to dissolve in a mixture of the acids, then the acid was neutralized with alkaline carbonate, and the iodine set free estimated by means of arsenious acid. The molecular proportions of iodic acid to iodine as found were as follows:

HIO_3 : I
1 : 4.02
1 : 4.07

The same proportions were obtained by direct titration of iodic acid against a solution of iodine in hydrochloric acid of known strength. The operation was performed in a flask, a definite quantity of iodic acid being first introduced and then the solution of iodine added from a burette until, upon shaking the flask, the presence of free iodine was indicated by the characteristic color given to chloroform.

The molecular proportions found were:

HIO_3 : I
1 : 4.02
1 : 4.06

These results, it will be seen, are in complete accordance with those obtained by the former method and indicate the following reaction:

$$HIO_3 + 2I_2 + 5HCl = 3H_2O + 5ICl.$$

The equation obtained above for the reaction between iodic acid, potassium iodide, and hydrochloric acid, viz.:

$$HIO_3 + 2KI + 5HCl = 3H_2O + 2KCl + 3ICl,$$

can be derived directly by a combination of the ordinary equation, in which iodine is set free,

$$[5KI + HIO_3 + 5HCl = 3H_2O + 5KCl + 3I_2]2,$$

with the equation just established,

$$[HIO_3 + 2I_2 + 5HCl = 3H_2O + 5ICl]3,$$

in which the iodine reacts upon iodic acid. This fact supports the assumption that the effect of a reducing agent upon an excess of iodic acid in presence of hydrochloric acid is to set free iodine which then dissolves in a mixture of the two acids to form iodine monochloride.

Iodine has apparently no effect upon either acid taken singly, and there is nothing in these experiments to show whether the action of the iodine on the iodic acid in the mixture of the

two acids is in the first instance of an oxidizing or reducing nature. It may be that the iodic acid is first reduced to a lower oxide, as has been previously suggested, or that it is oxidized to periodic acid. The first condition is expressed in equations I, and the latter in equations II, from which it is seen that either assumption agrees with the equations just established.

$$\text{I.}\left\{\begin{array}{l} 2HIO_3 + I_2 + 2HCl = I_4O_4 + 2H_2O + 2ICl \\ I_2O_4 + 3I_2 + 8HCl = 4H_2O + 8ICl \\ \text{Combined : } 2HIO_3 + 4I_2 + 10HCl = 10ICl + 6H_2O \end{array}\right\}$$

$$\text{II.}\left\{\begin{array}{l} 2HIO_3 + 2H_2O + 2I_2 = 4HI + H_2O + I_2O_7 \\ I_2O_7 + 4HI + 10HCl = 7H_2O + 6ICl + 2Cl_2 \\ \qquad 2Cl_2 + 2I_2 = 4ICl \\ \text{Combined : } 2HIO_3 + 4I_2 + 10HCl = 10ICl + 6H_2O \end{array}\right\}$$

In any case it is evident that the mixture of iodine and iodic acid, both ordinarily oxidizing agents, is able to effect the decomposition of hydrochloric acid with the formation of iodine monochloride.

XXXIV

THE GENERATION OF CHLORINE FOR LABORATORY PURPOSES.

By F. A. GOOCH and D. ALBERT KREIDER.*

THAT chlorine may be generated in a state of greater or less purity, variable with the conditions of evolution, by the action of hydrochloric acid upon potassium chlorate has been shown by Pebal † and Schacherl, ‡ but the application of this fact to the practical generation of chlorine for the purposes of the laboratory has not to our knowledge been proposed. The desirability of an automatic generator from which an abundant flow of chlorine gas may be drawn at will or shut off without danger or inconvenience has led us to a study of the conditions most favorable to the safe evolution of chlorine by the action of the chlorate.

Pebal § showed that the gas evolved at ordinary temperatures from a mixture of potassium chlorate and sodium chloride acted upon by sulphuric acid diluted with twice its volume of water consists of chlorine and chlorine dioxide in nearly equal proportions. Schacherl || found that when potassium chlorate was acted upon by hydrochloric acid diluted with twice its own volume of water the yield of chlorine was about 46 per cent or 57 per cent of the mixed gases according as the chlorate was granular or in fine powder; that hydrochloric acid of half-strength yielded a gas containing nearly 60 per cent of chlorine, and that the proportion of chlorine rose nearly to 68 per cent when the gas was passed

* From the Am. Jour. Sci., xlviii, 166.
† Ann. Chem. (Liebig), clxxvii, 1.
‡ Ibid., clxxxii, 197.
§ Loc. cit. || Loc. cit.

through concentrated hydrochloric acid and then washed with water; that the chlorate when acted upon by the strongest hydrochloric acid cooled to 0° C. and then warmed only enough to start the action yielded a gas carrying 87 per cent of chlorine; and that when a solution of potassium chlorate was permitted to flow into hot strong hydrochloric acid the free chlorine constituted nearly 95 per cent of the mixture. So it appears that the highest yield of chlorine resulted when the solution of the chlorate entered gradually the hot strong acid — a condition not easily attained in an automatic generator.

The fact that chlorine dioxide is so easily decomposed by heat into chlorine and oxygen naturally suggests the possibility of increasing the proportion of chlorine evolved in the first instance by working at the highest temperatures practically attainable under the conditions. In order, however to secure a temperature approaching the boiling point of water it is necessary to reduce somewhat the strength of the hydrochloric acid acting (in order to avoid the evolution of hydrochloric acid gas and the consequent interference with the regular automatic action of the generator), thus sacrificing the advantage naturally attending the use of acid of the highest degree of concentration. Upon experiment we find that acid of half-strength (sp. gr. 1.10) can be made to yield a very satisfactory proportion of chlorine. We have employed in our work potassium chlorate fused (best in platinum) and cast in sticks or broken into coarse lumps. A small Kipp's apparatus, holding about a half-litre of liquid in the two lower chambers, makes a convenient generator, and the requisite temperature may be secured by wrapping the two lower chambers with flexible metallic tubing through which steam is driven, or, with equal convenience, by simply standing the whole apparatus in heated water. When the simple precaution is taken to heat the acid to 60° or 70° C. before allowing it to come slowly into contact with the fused chlorate no difficulty whatever is met with in the practical automatic working of tl g ld acid is

permitted to act upon the chlorate it becomes charged more or less with the chlorine dioxide and a subsequent rise of temperature may cause dissociation of the explosive gas with sufficient suddenness to expel the liquid from the generator with considerable violence. The gas evolved directly from the generator is never pure chlorine. To determine the relative proportions of chlorine and chlorine dioxide (the sole products of the action according to Pebal) the gas as it issued from the generator was passed through two pipettes fitted with glass stop-cocks and joined to one another. After allowing a reasonable time for the complete expulsion of air from the pipettes the stop-cocks were closed, and the pipettes were disconnected from one another and from the generator. The gas contained in one of the pipettes was slowly forced by means of carbon dioxide through a solution of potassium iodide; that in the second pipette was driven slowly by means of carbon dioxide through a hard glass tube filled with asbestos and heated to redness by a Bunsen burner, and then passed through a solution of potassium iodide. The iodine set free in each case was determined in the acidified solution by standard sodium thiosulphate, and the difference in the amounts of iodine found was attributed to the action of the oxygen of the chlorine dioxide. It was assumed that the gas filling the pipettes ranged in line was homogeneously distributed, and this assumption is probably nearly enough true for the purpose of this discussion. The temperature of the acid in the generator was determined by inserting a thermometer in the lowest chamber of the generator, so that the indication for the point of action is only approximate.

In two experiments made with acid of half-strength and at indicated temperatures of 80° and 81° the chlorine in the gas amounted to 81.6 per cent and 84 per cent respectively of the mixture. In a comparison experiment made with the strongest acid heated to 50° — the highest temperature attainable without evolution of the hydrochloric acid gas — the yield of chlorine was 77.3 per cent. It is evident that the acid of

half-strength acting at 80° is productive of a more favorable yield than the strongest acid at 50°.

Temperatures very much higher than those employed can hardly be secured continually under the conditions of work, and yet it is plain that a considerable amount of the oxide still accompanied the chlorine. We made the attempt, therefore, to accomplish the destruction of the oxide by passing the mixed gases as they issued from the generator through a small wash-bottle containing a hot saturated solution of manganous chloride in strong hydrochloric acid, making use of a device previously employed in this laboratory for the decomposition of nitric acid and chloric acid.* The results of several experiments conducted in this manner are recorded in the accompanying statement. The gas after leaving the manganous chloride passed through a small wash-bottle filled with water, was dried by calcium chloride, collected in the pipettes arranged in train, and analyzed by the method previously described.

Strength of hydrochloric acid.	Temperature of acid.	Temperature of the solution of $MnCl_2$.	Bubbles of gas passing the wash-bottle per second.	Per cent of chlorine.
	°	°		
Sp. gr. 1.1	83	90	5–6	87.5
" 1.1	83	90	4–6	89.5
" 1.1	70–80	90	1–2	96.4
" 1.1	87.5	90	3	98.6
" 1.1	83	90	3	96.9

It is evident from these figures that the efficiency of the manganous chloride is considerable and naturally most manifest when the current of gas is slow. Indeed, during the passage of gas through the manganous salt small bubbles of chlorine are evolved from the entire surface of the liquid. The washed gas is pure enough for most laboratory purposes, but if chlorine perfectly free from chlorine oxide is desired it may be obtained by passing the washed gas through a hard glass tube filled with asbestos and heated by a Bunsen flame.

* Am. Jour. Sci., xliv, 117; xlvi, 231. This volume, pp. 132, 219.

In the exceptional cases in which the ignition tube is used it is well to keep in mind the fact that in starting the generator the acid should not be thrown in too great quantity upon the chlorate at first, lest an unusually large proportion of the dioxide be liberated, which may cause a slight explosion in the ignition tube. Should such be the case, however, the liquid in the wash-bottle will prevent the extension of the explosion to the gas in the generator proper, and the insertion of the wash-bottle should never be omitted when the ignition tube is to be put to use. So long as it is kept hot we have never found the apparatus other than perfectly manageable, safe, and automatic in action.

Inasmuch as a single gram of potassium chlorate produces approximately a half-liter of chlorine, and a cubic centimeter more than a liter, it is obvious that a very compact generator may be capable of delivering a considerable supply of the gas, and we have found the diminutive apparatus shown in the accompanying figure an exceedingly convenient addition to the furnishings of the laboratory table when chlorine is needed frequently and in small amounts. This little generator is easily made of a side-neck test-tube, funnel tube, stopper, glass stop-cock, and flask. The upper chamber of the test-tube, which is constricted near the middle, holds easily ten grams of the fused chlorate, and when the outer flask is filled with hot water the automatic action is satisfactory for a considerable length of time. A little wash-bottle containing a hot saturated solution of manganous chloride in strong hydrochloric acid is a desirable addition when a purer gas is needed than that delivered directly from the generator, and the attachment of the ignition tube makes it possible to secure the chlorine entirely free from chlorine oxide, though carrying, of course, some free oxygen.

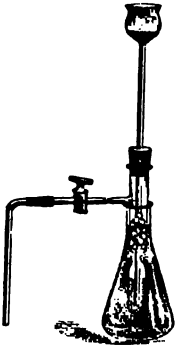


FIG. 9.

XXXV

THE REDUCTION OF ARSENIC ACID BY THE ACTION OF HYDROCHLORIC ACID AND POTASSIUM BROMIDE.

By F. A. GOOCH and I. K. PHELPS.*

It was shown in a former paper from this laboratory † that arsenic acid may be easily reduced by the simultaneous action of hydrochloric acid and potassium iodide, and more recently ‡ this reaction has been successfully applied to the rapid detection of arsenic in presence of antimony and tin, and of antimony and tin associated with arsenic. This paper is the account of work in the course of which it became evident that the action of hydrobromic acid upon arsenic acid is so similar to that of hydriodic acid that potassium bromide may with propriety, and even with advantage, be substituted for the iodide in the process of reduction.

The apparatus which we have used in this work is similar to that employed previously, and is essentially a Mohr's distillation apparatus — consisting of a small flask, of from 25 cm^3 to 50 cm^3 capacity, fitted by means of a pure rubber stopper to a pipette which was bent, drawn out at the lower end, and dipped into a test-tube supported and cooled in an Erlenmeyer flask nearly filled with water. The arsenic was introduced into the flask in the form of the pure crystallized dihydrogen potassium arseniate which was dissolved with 3 grm. of potassium bromide in 5 cm^3 of water, and 5 cm^3 of hydrochloric acid of full strength (sp. gr., 1.20) were added. The end of the pipette tube was dipped into 5 cm^3 of

* From Am. Jour. Sci., xlviii, 210.

† Gooch and Danner, Am. Jour. Sci., xlix, 208. This volume, p. 86.

‡ Gooch and Hodge, Am. Jour. Sci., xlvii, 199. This volume, p. 231.

hydrochloric acid of half strength contained in this test tube used as a receiver, and the distillation was carried on until the liquid in the flask had almost entirely passed to the receiver. The residue was treated with 10 cm^3 of the strongest hydrochloric acid, and the distillation was repeated with the modification that this time the condensation was effected by passing the volatile material into 10 cm^3 of water, so that the liquid in the receiver at the end of this operation should have the acidity of hydrochloric acid of half strength. This process of treating the residue with the strongest hydrochloric

	Arsenic taken as H_3AsO_4	Antimony taken as H_3SbO_4	Tin taken as $SnCl_4$	Precipitation by H_2S in successive distillates after treatment with $SnCl_2$	Precipitation by H_2S in the residue dissolved in water.
	grm.	grm.	grm.		
(1)	. . .	. . .	. . .	I. None.	None.
(2)	. . .	. . .	. . .	I–X. None.	Faint coloration.
(3)	0.0001	. . .	. . .	I. Found. II. None.	None.
(4)	0.0010	. . .	. . .	I. Found. II. None.	None.
(5)	0.0100	. . .	. . .	I–II. Found. III. None.	None.
(6)	0.1000	. . .	. . .	I–III. Found. IV. None.	Faint coloration.
(7)	0.4000	. . .	. . .	I–VI. Found. VII. None.	Orange precipitation.*
(8)	1.0000	. . .	. . .	I–X. Found. XI. None.	Orange precipitation.*
(9)	. . .	0.4000	. . .	I. None.	Large.
(10)	0.0001	0.4000	. . .	I–II. Found. III. None.	Large.
(11)	0.0001	0.0001	. . .	I. Found. II. None.	Distinct color.
(12)	0.0010	0.0001	. . .	I. Found. II. None.	Distinct color.
(13)	0.0100	0.0001	. . .	I–II. Found. III. None.	Distinct orange.
(14)	. . .	. . .	0.4000	I. None.	Large.
(15)	0.0001	. . .	0.4000	I–II. Found. III. None.	Large.
(16)	0.0001	. . .	0.0001	I. Found. II. None.	Distinct color.

acid and distilling was continued until arsenic ceased to be discoverable in this distillate. At the beginning of the

* Subsequently identified as antimony sulphide by depositing the metal on platinum.

distillation bromine is liberated and collects in this distillate; but later, as the arsenious chloride volatilizes and condenses again, the color of the bromine in the distillate vanishes with the simultaneous reconversion of the arsenic to the higher form of oxidation. In such a solution, especially if it is not very hot, hydrogen sulphide precipitates the arsenic only slowly, but the addition of a little stannous chloride dissolved in hydrochloric acid of half-strength to the hot solution reduces the arsenic to the lower form of oxidation and prepares the way for the immediate precipitation of arsenious sulphide by hydrogen sulphide. Antimonic acid is likewise reduced under the conditions of the distillation; but, as Koehler has shown,* neither small amounts of antimony and tin, which if present originally may pass partially to the distillate, nor the tin added to effect the reduction of the arsenic finally, will be precipitated by hydrogen sulphide under the existing conditions of temperature and acidity.

The results of experiment are recorded in the accompanying table.

Whenever antimony was introduced intentionally it was taken in the form of antimonic acid produced by oxidizing by bromine in alkaline solution tartar emetic purified by boiling with hydrochloric acid until the distillate contained no trace of arsenic. The stannic chloride employed was purified by boiling in strong hydrochloric acid with potassium bromide.

It will be seen that no indication was given by hydrogen sulphide either in the distillate or residue when the hydrochloric acid (10 cm^3) and the potassium bromide (3 grm.) were treated in blank. When the bromide was treated in blank ten times successively no indication was obtained in any individual distillate, but the residue showed a trace of color which was apparently intensified by the action of hydrogen sulphide. This effect was slight and probably due to the prolonged action of the acid upon the rubber. It is not sufficient to interfere with the detection of 0.0001 grm. of antimony — as subsequent experiments showed.

* Zeitschr. anal. Chem., xxix, 192.

A single distillation, requiring but three or four minutes, proved to be sufficient for the complete volatilization of 0.0010 grm. of arsenic, two distillations were enough to remove 0.01 grm. and three 0.1 grm. of arsenic. In handling larger amounts of arsenic, 0.4 grm. or 1 grm., it became evident that the presumably pure arseniate actually contained a trace of antimony, and the efficiency of the bromide treatment in effecting the detection of a little antimony in presence of a large amount of arsenic is clearly shown. It is plain that while the presence of large amounts of antimony and tin tend to diminish the rapidity of volatilization of the arsenic, the detection of 0.0001 grm. of arsenic is always sure, and that antimony and tin if originally present in appreciable amount will always be discoverable in the residue.

In a comparison of the results of these experiments with those recorded in the former paper describing the reduction by means of potassium iodide, it appears that in general fewer distillations are needed to effect the transfer of the arsenic to the distillate when the bromide is employed — a condition of affairs which is doubtless due to the fact that in the former treatment an insoluble and somewhat refractory precipitate of arsenious iodide is formed when large amounts of arsenic are present, while the bromide causes no precipitation of the arsenic, and interferes in no way with the distillation of the reduced product.

For the production of a definite amount of electrolytic iron two different courses are open to us. Either a weighed amount of a pure iron salt, as ammonio-ferrous sulphate, may be taken and the iron completely precipitated by electrolysis; or an indefinite quantity of the salt may be taken and subjected to electrolysis for a time, and the amount of iron determined by weighing the electrolytic deposit. After some preliminary trials, this second method has recommended itself to me as being much more rapid than the first-mentioned method and also free from some manipulatory details which render the first difficult to be done with exceeding accuracy.

Some experiments were therefore undertaken to compare the amount of iron determined by direct weighing of the electrolytic deposit with the amount determined by titration of the solution of this same iron with potassium permanganate. The details of the experiments were as follows. The solution of potassium permanganate was first accurately standardized with ammonium oxalate which had been shown to give identical results with those obtained by the use of lead oxalate. About 10 grams of ammonio-ferrous sulphate were dissolved in about 150 cubic centimeters of water, 5 cubic centimeters of a saturated solution of potassium oxalate were added, and then the whole was heated with a considerable quantity of solid ammonium oxalate until a clear solution was obtained. This solution was decomposed in a beaker between two platinum electrodes, the iron being deposited on a piece of platinum foil of a size convenient to be inserted in a rather large weighing bottle, in which it was weighed both before and after the electrolysis. From $1\frac{1}{4}$ to $1\frac{1}{2}$ hours, with a current of 2 ampères, was in general found to be sufficient to precipitate from 0.4 to 0.5 grams of pure iron, and it was found unadvisable to use a current much stronger than 2 ampères, since a higher current showed a tendency to render the deposit less smooth and compact. After washing, drying, and weighing in the usual way, the iron was dissolved in hydrochloric acid, the weighing bottle being used instead of the small flask ordinarily employed in this

operation, the oxidized iron was reduced with zinc, and finally titrated with the potassium permanganate solution in presence of sulphuric acid and a large amount of water.

The following table shows the results obtained, the first column giving the weight of the electrolytic deposit of iron, and the second the weight of iron found in the solution of the preceding upon titration with potassium permanganate previously standardized on ammonium oxalate.

I.	II.	Difference.
0.4357	0.4364	0.0007+
0.3551	0.3559	0.0008+
0.2552	0.2550	0.0002−
0.2898	0.2890	0.0008−
0.1590	0.1599	0.0009+
0.3528	0.3534	0.0006+
0.4498	0.4494	0.0004−
0.5086	0.5085	0.0001−
0.4462	0.4457	0.0005−
0.4226	0.4222	0.0004−
0.5170	0.5165	0.0005−

These results show that the standard of potassium permanganate as determined from pure iron differs very slightly from that obtained with the ammonium oxalate, but the standard obtained in the former way would under ordinary conditions be more satisfactory for work in iron analysis than the latter. A simple and rapid method, then, for standardizing the potassium permanganate solution would be to determine its strength, first, by comparison with electrolytic iron in the manner above described, and then by immediate titration to determine the exact amount of iron in each cubic centimeter of a solution of ferric chloride reduced as usual with zinc. This being ascertained, the ferric chloride solution can be employed at any time for the standardization of potassium permanganate.

XXXVII

THE DETECTION AND APPROXIMATIVE ESTIMATION OF MINUTE QUANTITIES OF ARSENIC IN COPPER.

By F. A. GOOCH and H. P. MOSELEY.*

SANGER'S recent successful application of the Berzelius-Marsh process to the quantitative determination of arsenic in wall-papers and fabrics,† by the comparison of test mirrors with standard mirrors carefully prepared under the conditions of the test, opens the way, naturally, to the similar estimations of minute amounts of arsenic in any substances which may be submitted to the process immediately or after suitable preparation.

The need of a rapid and at the same time trustworthy method for the determination of traces of arsenic in copper has led us to a study of the application of Sanger's process to this special case.

It has been shown by Headden and Sadler‡ that the presence of copper in the Marsh generator is instrumental in holding back the arsenic, and our own experience is similar. It is obvious, therefore, that means must be employed for the complete removal of the copper from the arsenic before the solution of the latter is put into the reduction-flask. So far as our experience goes, there is no method by which arsenic may be removed from copper easily, and without loss, aside from those methods which depend upon the volatility of arsenious chloride from solution in strong hydrochloric acid, and of such methods we give the preference on the score of rapidity in execution, accessibility of pure materials, and compactness

* From Am. Jour. Sci., xlviii, 292. † Am. Chem. Jour., xiii, 431.
‡ Am. Chem. Jour., vii, 342.

of apparatus, to a process recently developed in this laboratory * and based upon the simultaneous action of strong hydrochloric acid and potassium bromide upon the salt of arsenic.

To get the copper into condition for the application of the process of separation from arsenic we find it sufficient to dissolve an amount not exceeding one gram in nitric acid somewhat diluted with water, to add to the solution two or three cubic centimeters of strong sulphuric acid, and to evaporate the liquid until fumes of the sulphuric acid are disengaged abundantly. A single treatment of this sort serves to remove the nitric acid so completely that no interference with the normal action of the Marsh apparatus is apparent in the subsequent operation. The residue after concentration is diluted with water to about 5 cm^3 and washed into the distillation flask with an amount of the strongest hydrochloric acid (sp. gr., 1.20) equal to that of the remainder of the liquid. It is desirable that the entire volume of the liquid should not much exceed 10 cm^3. The flask which has a capacity of forty or fifty cubic centimeters, is inclined at an angle of about 45° and joined by means of a pure rubber stopper to a bent pipette which serves as a distillation tube. The lower end of the vertical limb of the pipette dips beneath the surface of about 5 cm^3 of hydrochloric acid of half strength contained in a test-tube which is cooled and supported by water nearly filling an Erlenmeyer flask. A single gram of potassium bromide is introduced, and the distillation (which may be completed in three or four minutes) is pushed nearly to dryness. The flask is washed out, another portion of potassium bromide is introduced, and the first distillate is introduced and redistilled as before excepting that the condensation is this time effected in pure water. This second operation serves merely to hold back traces of copper carried over in the first distillation, but experiment has shown that the addition of the potassium bromide in the second distillation is quite as necessary as in the first, since the bromine liberated in the process has the effect of reoxidizing the arsenic in the receiver and so making

* Gooch and Phelps, Am. Jour, Sci., xlviii, 216. This volume, p. 265.

that element non-volatile under the conditions until the reducing agent is again introduced. The free bromine in the final distillate must be re-converted to hydrobromic acid before the contents of the receiver may be introduced into the reduction-flask, and we find that this effect may be most easily and unobjectionably accomplished by the addition of a little stannous chloride dissolved in hydrochloric acid of half-strength and purified from arsenic by prolonged boiling. Incidentally and simultaneously the arsenic is reduced to the arsenious form, and, though Sanger has shown that minute amounts of arsenic are completely eliminated from the solution in the reduction flask when that element is introduced in the higher form of oxidation, it is our experience that the rapidity of elimination of the arsenic is so increased by the introduction of the small amount of stannous chloride needed to bleach the bromine that the mirror appears in from five to ten minutes and is practically complete in half an hour, especially if the precaution is taken to add a little more stannous chloride, according to Schmidt's suggestion* after the operation has been in progress about twenty minutes.

It will be remembered that Schmidt has shown that the addition of stannous chloride to the Marsh apparatus in action not only does not effect the retention of arsenic, as many other metallic salts do, but actually brings about the final evolution in the form of the hydride of that portion of the arsenic which may have been deposited during the process in elementary form upon the zinc.

We have used the Sanger apparatus in form essentially unchanged; but we find it advantageous to fill the reserve generator with zinc coated with copper by the action of a solution of copper sulphate, instead of with pure zinc, since in this way the zinc is made more sensitive to the action of the dilute sulphuric acid, while the presence of copper (which is of course out of the question in the reduction-flask) can be of no disadvantage in the reserve generator and might even serve a useful end in fixing traces of arsenic if the zinc and acid

* Zeitschr. anorg. Chem., i, 353.

employed were not absolutely free from that element. In the formation of the mirror too, it has proved to be an advantage to enclose the portion of the glass tube to be heated in a short thin tube of iron or nickel slightly larger than the glass tube and kept from contact with it except at the ends, which are notched and bent inward. By keeping the outer tube of metal at a low red heat it is possible to diminish the tendency, which shows more particularly when the amounts of arsenic are fairly large, toward the formation of a double mirror corresponding to the allotropic conditions of the arsenic. The exigency compels, moreover, the substitution of hydrochloric acid for the sulphuric acid usually employed in the reduction flask; but though the opinion is current that hydrochloric acid introduces difficulties in the Marsh test, we have been unable to discover any evidence of the formation of a zinc mirror in the ignition tube or to note other unfavorable action due to the use of pure hydrochloric acid. It is, of course, obvious that the hydrochloric acid used must be actually free from arsenic (as was ours) and not merely nominally so, as is often the case with the so-called arsenic-free hydrochloric acid of commerce.

Copper taken, in grams.	Arsenic taken, in milligrams.	Mirror estimated (by comparison with standard mirror) in milligrams.	Error, in milligrams.
None.	None.	None.	None.
0.7	None.	None.	None.
0.5	0.005	0.003	0.002–
0.5	0.011	0.013	0.002+
0.35	0.020	0.015	0.005–
0.3	0.030	0.030	None.
0.43	0.040	0.035	0.005–
0.44	0.050	0.040	0.010–

The copper for our test experiments was prepared free from arsenic by electrolyzing in ammoniacal solution the purest copper sulphate obtainable and stopping the deposition before the solution had become exhausted. In this manner we were able to procure copper in which we failed to detect arsenic.

This copper was dissolved in nitric acid, arsenic in the higher condition of oxidation was added, and the process of the separation of the arsenic from the copper and conversion to the mirror carried out in the manner described. The results obtained are recorded in the preceding table.

It is plain from these results that the method is capable of detecting sharply minute amounts of arsenic in copper and of effecting the estimation of quantities less than 0.05 mg. with some approximation to accuracy. There is, as Sanger has pointed out, a good deal of variation even in standard mirrors made with all possible care and precaution, and in the estimation of mirrors containing as much as 0.05 mg. of arsenic the uncertainty of comparison as well as the actual variation of the mirror is considerable.

When a sample of copper is under test which may contain more than 0.05 mg. of arsenic it is desirable to introduce into the reduction-flask the measured solution containing the arsenic gradually and in definite portions, and to judge by the formation of the mirror in an interval of ten minutes after the introduction of portions of this test solution whether it is wiser to add the entire solution or to estimate the arsenic in the entire solution from that found in an aliquot portion.

We append the results of the analysis of several samples of commercial copper, all of which were electrolytic, and of which the last two represented, presumably, the very purest electrolytically refined copper obtainable commercially.

	Copper taken, grams.	Arsenic found, milligrams.	Percentage of arsenic.
Sample A	0.3	0.015	0.005
Sample B	0.3	0.030	0.010
Sample C	1	0.018	0.0018
	1	0.015	0.0015
Sample D	1	0.005	0.0005
	1	0.005	0.0005

XXXVIII

AN IODOMETRIC METHOD FOR THE ESTIMATION OF TELLURIC ACID.

By F. A. GOOCH and J. HOWLAND.*

In his valuable and extended study of possible volumetric methods for the estimation of tellurium, Brauner† has investigated the action of iodine upon an alkaline tellurite and finds that the oxidation is slow and incomplete at ordinary temperatures, while at 100° C. and in presence of a sufficient excess of iodine complete oxidation takes place, though the difficulty of estimating the excess of iodine not directly utilized in the reaction is so great as to render the method practically inapplicable to the determination of tellurium. The difficulty in effecting oxidation in alkaline solution naturally suggests the reversal of the reaction in an attempt to reduce telluric acid by the action of hydriodic acid in acid solution. Upon putting the matter to the test we find the reduction of telluric acid does take place, but we have been unable to prevent its going too far. Thus, on boiling a solution containing 10 cm^3 of sulphuric acid of half-strength, 3 grm. of potassium iodide in 90 cm^3 of water and a little more than 0.1 grm. of telluric acid, the liquid darkened, deposited dark gray crystalline scales, and evolved iodine which, when collected and titrated with sodium thiosulphate, proved to be twenty per cent in excess of the theoretical yield, assuming that the reduction should result in the production of tellurous acid. A similar experiment made in like manner excepting that the liquid was heated for fifteen minutes in a closed bottle on the water-bath instead of being subjected to boiling, with

* From Am. Jour. Sci., xlviii, 375.

† Jour. Chem. Soc., lix, 58, 238.

the idea that the presence of the free iodine might tend to prevent excessive reduction of the tellurium, indicated a yield of free iodine about six per cent in excess of what it should be if tellurous acid is the sole product of reduction. In this case the titration of the free iodine was made by sodium thiosulphate in the presence of the reduced tellurous acid, but we found by independent experiment that the determination of free iodine associated with tellurous acid may be accomplished with a fair degree of accuracy provided the solution be cold and dilute, and the final reaction secured by adding the thiosulphate in slight excess and restoring the color permanently by standard iodine. Even under the most favorable conditions the tellurous acid is somewhat acted upon by sodium thiosulphate even before the free iodine is entirely bleached and the reaction in the reverse titration by standard iodine is slow in coming, though finally definite; but if the solution is hot the thiosulphate precipitates tellurium in flocky condition.

The excessive action of the iodide suggested the substitution of potassium bromide — an agent which proved of value in reducing arsenic acid as described in a recent paper from this laboratory — and, the preliminary experimentation proving to be encouraging, we set about the preparation of telluric acid of definitely known strength. We weighed out accurately tellurous oxide, prepared by oxidizing presumably pure crystallized tellurium with nitric acid and igniting the product at a low red heat, dissolved the weighed oxide in a few cubic centimeters of a strong solution of potassium hydroxide, precipitated the tellurous acid by the careful addition of dilute sulphuric acid, and dissolved the precipitate in 10 cm^3 of sulphuric acid of half-strength. The solution thus obtained was treated with potassium permanganate in excess, the manganic oxide and the excess of permanganate were bleached by oxalic acid added to the hot solution, and the excess of oxalic acid was destroyed by the addition of a dilute solution of the permanganate until the faintest possible blush of color appeared. For the experiments involving the treatment of the larger amounts of tellurium every preparation

was made individually in the manner described; for the experiments with smaller amounts a single preparation was made and the solution thus obtained was diluted to a half litre and portions of this standard solution were drawn from a burette as occasion required.

The equivalent of the so-called element tellurium is, as Brauner has shown,* so variable with the mode of determining that constant and the preparation of material that we employed a preparation of tellurous oxide which had been tested as to its equivalent weight by Brauner's excellent method of oxidation by potassium permanganate. The results of these tests are recorded in the accompanying table. In series I the alkaline solution of the oxide was diluted to 100 cm^3 and oxidation was effected in it by standard permanganate added in excess. Sulphuric acid of half-strength was added to neutralization and then 5 cm^3 more, the liquid

TeO_2 taken.	Oxygen required for oxidation.	Molecular weight of TeO_2 when O = 16.	Mean.
Series I.			
grm.	grm.		
0.1200	0.01202	159.7	158.65
0.0783	0.00785	159.6	
0.0931	0 00940	158.4	
0.1100	0.01119	157.3	
0.0904	0.00909	159.1	
0.1065	0.01078	157.8	
Series II.			
0.0910	0.00914	159.3	159.08
0.0910	0.00910	160	
0.0911	0.00924	157.7	
0.0913	0.00915	159.6	
0.0912	0.00915	159.5	
0.0914	0.00923	158.4	

was heated, a solution of oxalic acid of known value was introduced to an amount slightly in excess of that needed to destroy the manganic oxide and excess of permanganate, and the surplus of oxalic acid was removed by standard perman-

* Jour. Chem. Soc., 1889, 382.

ganate. In series II the alkaline solution of the oxide was neutralized with dilute sulphuric acid and 1 cm^3 of sulphuric acid of half-strength was added. The oxidation was accomplished from this point exactly as in series I, the only difference being that it took place in the presence of a slight excess of sulphuric acid instead of in alkaline solution. The permanganate used in both series was standardized ultimately against lead oxalate.

The mean value of these determinations assigns to the tellurous oxide which we employed a molecular weight of about 159 and to the element tellurium an atomic weight of 127, when oxygen is 16. Brauner advocates the application of a correction made necessary by the excessive decomposition of the permanganate in the oxidation; but inasmuch as the oxidation in series I took place in alkaline solution under conditions in which we have no absolute proof that unused oxygen is liberated to any considerable degree from the permanganate, while in series II the excess of sulphuric acid was purposely restricted to the lowest limit — the sulphuric acid having been shown in a previous paper from this laboratory * to be the chief agent in inducing the excessive decomposition of the permanganate — we incline, provisionally at least, to accept in this case the result of the analysis without correction.

In the test experiments the telluric acid, prepared in the manner described, was introduced into the apparatus for distillation with 3 grms. of potassium bromide, care being taken to insure in the 50 cm^3 or more of liquid the presence of 10 cm^3 of sulphuric acid of half strength. A current of carbon dioxide was passed through the apparatus, the solution was boiled to set free the bromine which was absorbed in potassium iodide and estimated by standard sodium thiosulphate. In handling the larger amounts of tellurium we found it desirable to make the preparation of the telluric acid in the distilling flask and to boil out the oxygen and ozone set free in the preparation before proceeding with the operation. The

* Gooch and Danner, Am. Jour. Sci., xliv, 301. This volume, p. 145.

apparatus which we used consisted of a Voit's gas-washing flask, with sealed-in inlet tube and ground-in outlet tube, used as the distillation flask, to which was joined by a sealed joint the inlet tube of a Drexel washing bottle to the outlet tube of which was sealed a Will and Varrentrapp absorption apparatus. The washing bottle and attached bulbs contained a solution of 3 grams of potassium iodide and the former was kept cool by standing it during the distillation in a vessel of cold water. The absorption of the bromine took place almost entirely in the bottle, only traces of iodine being set free in the bulbs. The results of our experiments are recorded in the accompanying statement; Te = 127, O = 16.

Exp.	Initial volume.	Final volume.	TeO_2 taken.	TeO_2 found.	Error.
	cm_3	cm_3	grm.	grm.	grm.
(1)	50	20	0.0102	0.0098	0.0004–
(2)	50	20	0.0102	0.0099	0.0003–
(3)	50	20	0.0102	0.0098	0.0004–
(4)	50	20	0.0102	0.0098	0.0004–
(5)	100	40	0.1000	0.0994	0.0006–
(6)	80	40	0.1001	0.1001	0.0000
(7)	100	20	0.1002	0.1001	0.0001–
(8)	50	20	0.1000	0.1003	0.0003+
(9)	50	25	0.5011	0.5008	0.0003–
(10)	50	25	0.5002	0.5006	0.0004+
(11)	50	25	0.5000	0.4998	0.0002–
(12)	50	20	0.5000	0.4994	0.0006–

The results of experiment agree fairly well with one another and with theory based upon the assumption that the atomic weight of the tellurium which we employed was 127. It is evident that the reducing action of the hydrobromic acid developed in the distillation is regular and that that agent is well adapted to the reduction of telluric acid to tellurous acid. The formation of tellurium tetrabromide in the concentrated acid liquid makes it impossible to tell by the color when all the bromine has been distilled, but the evidence of the experiments goes to show that the boiling of the liquid from a volume of 50 cm^3 to 25 cm^3 is sufficient, while concentration from 100 cm^3 to 20 cm^3 apparently does no harm.

XXXIX

THE PREPARATION OF PERCHLORIC ACID AND ITS APPLICATION TO THE DETERMINATION OF POTASSIUM.

By D. ALBERT KREIDER.*

VARIOUS methods for the preparation of perchloric acid have been developed through the long felt want of a process in which the elements of time and danger would be reduced to a minimum and the product increased to quantities commensurate with the growing use of the acid in analytical chemistry. Most of these methods have been found impracticable because of the incidental formation of the dangerously explosive oxides of chlorine, or the time required in refining the product from the impurities introduced with the reagents employed.

Doubtless the best process thus far offered is that of Caspari,† which, however, is to an objectionable degree exacting of time and labor. The product has to be treated and re-treated for the removal of potassium and then for the extraction of the hydro-fluo-silicic-acid and at several stages is for this purpose to be left standing for from twenty-four to forty-eight hours. Under the most favorable circumstances it could not be prepared in less than five or six days, and during a great many hours of that time it requires close attention.

The great difficulty has always been with the necessity of a perfect separation of potassium from the perchloric acid, which has been prepared by the ignition of the potassium chlorate. If, for the manufacture of the perchlorate, the chlorate of sodium — which, if not upon the shelves of every

* From Am. Jour. Sci. xlix, 443.

† Zeitschr. angew. Chem., 1893, 68.

laboratory, is nevertheless in the market, almost, if not entirely free of potassium — be used instead of the potassium salt, the complete removal of the base will be unessential; since its presence in the determination of potassium will exert no influence other than that which is beneficial. It is well known that because of its deliquescence and the almost equal solubility of sodium perchlorate with that of the chloride, its separation from the latter by recrystallization from an aqueous solution, as in the case of potassium, is impossible. But the insolubility of the chloride of sodium in strong hydrochloric acid, with the aid of the acid-proof Gooch crucible, affords a means for the liberation of the perchloric acid and the removal of the greater part of the sodium in one operation. Upon this basis, therefore, the following simple method was elaborated.

A convenient quantity of sodium chlorate, from 100 to 300 grms., is melted in a glass retort or round-bottomed flask and gradually raised to a temperature at which oxygen is freely, but not too rapidly evolved, and kept at this temperature till the fused mass thickens throughout, which indicates the complete conversion of the chlorate to the chloride and perchlorate, and requires between one and one-half to two hours: or the retort may be connected with a gasometer and the end of the reaction determined by the volume of oxygen expelled, according to the equation

$$2NaClO_3 = NaCl + NaClO_4 + O_2.$$

The product thus obtained is washed from the retort to a capacious evaporating dish where it is treated with sufficient hydrochloric acid to effect the complete reduction of the residual chlorate, which, if the ignition has been carefully conducted with well distributed heat, will be present in but small amount. It is then evaporated to dryness on the steam bath, or more quickly over a direct flame, and with but little attention until a point near to dryness has been reached, when stirring will be found of great advantage in facilitating the volatilization of the remaining liquid and in breaking up the

mass of salt. Otherwise the perchlorate seems to solidify with a certain amount of water, and removal from the dish, without moistening and reheating, is impossible.

After triturating the residue, easily accomplished in a porcelain mortar, an excess of the strongest hydrochloric acid is added to the dry salt, preferably in a tall beaker where there is less surface for the escape of hydrochloric acid and from which the acid can be decanted without disturbing the precipitated chloride. If the salt has been reduced to a very fine powder, by stirring energetically for a minute, the hydrochloric acid will set free the perchloric acid and precipitate the sodium as chloride, which in a few minutes settles, leaving a clear solution of the perchloric acid with the excess of hydrochloric acid. The clear supernatant liquid is then decanted upon a Gooch filter, through which it may be rapidly drawn with the aid of suction, the residue re-treated with the strongest hydrochloric acid and settled, the acid decanted, and the salt finally brought upon the filter where it is washed with a little strong hydrochloric acid. A large platinum cone will be found more convenient than the crucible, because of its greater capacity and filtering surface. When the filter will not hold all the sodium chloride, the latter after being washed may be removed by water or by mechanical means, with precautions not to disturb the felt, which is then ready for the remainder. Of course, if water is used, the felt had better be washed with a little strong hydrochloric acid before receiving another portion of the salt. This residue will be found to contain only an inconsiderable amount of perchlorate, when tested by first heating to expel the free acid and then treating the dry and powdered residue with 97 per cent alcohol, which dissolves the perchlorate of sodium but has little soluble effect on the chloride.

The filtrate, containing the perchloric acid with the excess of hydrochloric acid and the small per cent of sodium chloride which is soluble in the latter, is then evaporated over the steam bath till all hydrochloric acid is expelled and the heavy white fumes of perchloric acid appear, when it is ready for

use in potassium determinations. Evidently the acid will not be chemically pure, because the sodium chloride is not absolutely insoluble in hydrochloric acid; but a portion tested with silver nitrate will prove that the sodium, together with any other bases which may have gone through the filter, has been completely converted into perchlorate, and unless the original chlorate contained some potassium or on evaporation the acid was exposed to the fumes of ammonia, the residue of the evaporation of a portion is easily and completely soluble in 97 per cent alcohol and its presence is therefore unobjectionable. One cubic centimeter of the acid thus obtained gave on evaporation a residue of only 0.036 grm., which was completely soluble in 97 per cent alcohol.

Caspari's acid under similar treatment gave a residue in one case of 0.024 grms. and in another 0.047 grms. If, however, a portion of pure acid be required, it may be obtained by distilling this product under diminished pressure and, as Caspari has shown, without great loss, providing the heat is regulated according to the fumes in the distilling flask.

Some modification of the above treatment will be found necessary in case the sodium chlorate contains any potassium as an impurity, or if the latter has been introduced from the vessel in which the fusion was made. Under these circumstances the hydrochloric acid would not suffice for the removal of potassium, since a trace might also go over with the sodium and thus on evaporation a residue insoluble in 97 per cent alcohol be obtained. To avoid this difficulty, the mixture of sodium perchlorate and chloride, after being treated with hydrochloric acid for the reduction of the residual chlorate, being reduced to a fine powder, was well digested with 97 per cent alcohol, which dissolves the sodium perchlorate but leaves the chloride as well as any potassium salt insoluble. By giving the alcohol time to become saturated, which was facilitated by stirring, it was found on filtering and evaporating that an average of about 0.2 grm. of sodium perchlorate was obtained for every cubic centimeter of alcohol and that the product thus obtained was compara-

tively free of chlorides, until the perchlorate was nearly all removed, when more of the chloride seems to dissolve. This treatment with alcohol is continued until, on evaporation of a small portion of the latest filtrate, only a small residue is found. The alcoholic solution of the perchlorate is then distilled from a large flask until the perchlorate begins to crystallize, when the heat is removed and the contents of the flask quickly emptied into an evaporating dish, the same liquid being used to wash out the remaining portions of the salt. When the distillation is terminated at the point indicated, the distillate will contain most of the alcohol employed, but in a somewhat stronger solution, so that it requires only diluting to 97 per cent to fit it for use in future preparations. The salt is then evaporated to dryness on the steam bath and subsequently treated with strong hydrochloric acid for the separation of the perchloric acid.

One cubic centimeter of the acid prepared in this way, on evaporation gave a residue in one case of 0.0369 grms., and in another 0.0307 grm., completely soluble in 97 per cent alcohol, which was then ignited and the chlorine determined by silver from which the equivalent of perchloric acid in the form of salts was calculated as 0.0305 grm. By neutralizing the acid with sodium carbonate, evaporating, igniting in an atmosphere of carbon dioxide till decomposition was complete, collecting the oxygen over caustic potash, allowing it to act on hydriodic acid by intervention of nitric oxide, according to a process soon to be published, titrating the iodine liberated, with standard arsenic and calculating the equivalent of perchloric acid, after subtracting the amount of acid found in the form of salts, the amount of free acid per cubic centimeter proved to be 0.9831 grms.

The whole process, even when the separation with alcohol is necessary, cannot well require more than two days and during the greater part of that time the work proceeds without attention.

In applying perchloric acid, thus prepared, to the determination of potassium according to the treatment suggested

by Caspari * very satisfactory results were obtained. Briefly, the method is as follows: The substance, free from sulphuric acid, is evaporated to the expulsion of free hydrochloric acid, the residue stirred with 20 cm^3 of hot water and then treated with perchloric acid in quantity not less than one and one-half times that required by the bases present, when it is evaporated with frequent stirring to a thick, syrup-like consistency, again dissolved in hot water and evaporated with continued stirring till all hydrochloric acid has been expelled and the fumes of perchloric acid appear. Further loss of perchloric acid is to be compensated for by addition of more. The cold mass is then well stirred with about 20 cm^3 of wash alcohol — 97 per cent alcohol containing 0.2 per cent by weight of pure perchloric acid — with precautions against reducing the potassium perchlorate crystals to too fine a powder. After settling, the alcohol is decanted on the asbestos filter and the residue similarly treated with about the same amount of wash alcohol, settling and again decanting. The residual salt is then deprived of alcohol by gently heating, dissolved in 10 cm^3 of hot water and a little perchloric acid, when it is evaporatad once more with stirring, until fumes of perchloric acid rise. It is then washed with 1 cm^3 of wash alcohol, transferred to the asbestos, preferably by a policeman to avoid excessive use of alcohol, and covered finally with pure alcohol: the whole wash process requiring about 50 to 70 cm^3 of alcohol. It is then dried at about 130° C. and weighed.

The substitution of a Gooch crucible for the truncated pipette employed by Caspari will be found advantageous; and asbestos capable of forming a close, compact felt should be selected, inasmuch as the perchlorate is in part unavoidably reduced, during the necessary stirring, to so fine a condition that it tends to run through the filter when under pressure. A special felt of an excellent quality of asbestos was prepared for the determinations given below and seemed to hold the finer particles of the perchlorate very satisfactorily.

* Loc. cit.

A number of determinations made of potassium unmixed with other bases or non-volatile acids are recorded in the following table:

KCl taken.	Volume of filtrate.	$KClO_4$ found.	Error on $KClO_4$.	Error on KCl.	Error on K_2O.
grm.	cm^3	grm.	grm.	grm.	grm.
0.1000	54	0.1851	0.0008—	0.0004—	0.0003—
0.1000	58	0.1854	0.0005—	0.0002—	0.0002—
0.1000	51	0.1859	0.0000	0.0000	0.0000
0.1000	50	0.1854	0.0005—	0.0002—	0.0002—
0.1000	48	0.1859	0.0000	0.0000	0.0000
0.1000	52	0.1854	0.0005—	0.0002—	0.0002—

Considerable difficulty, however, was experienced in obtaining equally satisfactory determinations of potassium associated with sulphuric and phosphoric acids. As Caspari has pointed out, the sulphuric acid must be removed by precipitation as barium sulphate before the treatment with perchloric acid is attempted, and unless the precipitation is made in a strongly acid solution, some potassium is carried down with the barium. Phosphoric acid need not be previously removed; but to secure a nearly complete separation of this acid from the potassium, a considerable excess of perchloric acid should be left upon the potassium perchlorate before it is treated with the alcohol. When these conditions are carefully complied with, fairly good results may justly be expected. Below are given a number of the results obtained.

Compounds taken.	Vol. of filtrate.	$KClO_4$ found.	Error on $KClO_4$.	Error on KCl.	Error on K_2O.
grm.	cm^3	grm.	grm.	grm.	grm.
$KCl = 0.1000$					
$CaCO_3 = 0.13$	50	0.1887	0.0028+	0.0014+	0.0009+*
$MgSO_4 = 0.13$	82	0.1875	0.0016+	0.0008+	0.0005+*
$Fe_2Cl_6 = 0.05$	80	0.1861	0.0002+	0.0001+	0.0001+†
$Al_2(SO_4)_3 = 0.05$	80	0.1843	0.0016—	0.0008—	0.0005—†
$MnO_2 = 0.05$	92	0.1839	0.0020—	0.0010—	0.0006—†
$HNa_2PO_4 . 12H_2O = 0.40$	60	0.1854	0.0005—	0.0002—	0.0002—†

* The residue showed phosphoric acid plainly when tested.

† Only traces of phosphoric acid found in the residue.

In the last three experiments of the above table the amount of perchloric acid was about three times that required to unite with the bases present and the phosphoric acid subsequently found with the potassium was hardly enough to appreciably affect the weight, although its absolute removal was found to be impossible.

XL

THE ESTIMATION OF THE HALOGENS IN MIXED SILVER SALTS.

By F. A. GOOCH and CHARLOTTE FAIRBANKS.*

Known methods for the estimation of chlorine, bromine, and iodine in mixed silver salts depend either upon the reduction of the salts to metallic silver or their conversion to a single definite silver salt. The old but by no means ideal methods for the determination of chlorine and bromine in mixed silver chloride and bromide by reduction of the salts to silver in hydrogen at high temperatures or conversion to silver chloride in an atmosphere of chlorine are typical. Perhaps the best of all are the electrolytic method of Kinnicutt† for the reduction of the fused chloride and bromide, the battery process of Whitfield‡ which involves the electrolysis of the solution of the silver salts in potassium cyanide, and the method of Maxwell-Lyte § according to which the silver in the cyanide solution of the silver salts is thrown down by potassium iodide and sulphuric acid. Even in these processes there are points against which objection may be raised with reason. Thus, in the processes of Whitfield and Maxwell-Lyte it is next to impossible to secure complete and speedy solution of the dried silver salts in potassium cyanide without recourse to intermediate washing and treatment with nitric acid; and in Kinnicutt's method, which has been applied only to the analysis of the mixed chloride and bromide, difficulty is found in the speedy removal of all sulphuric acid from the spongy mass of silver formed in the reduction.

* From Am. Jour. Sci., 1, 27.
† Am. Chem. Jour., iv, 22.
‡ Am. Chem. Jour., viii, 421.
§ Chem. News, xlix, 3.

We have tried many experiments with a view to simplifying the analysis of the mixed silver salts. Ignition with mercuric cyanide according to Schmidt's method for sulphides;* treatment with cuprous chloride dissolved either in ammonia or in hydrochloric acid; the action of ferrous oxalate dissolved in potassium oxalate, Eder's † reagent; treatment with chromous chloride or chromous acetate; contact with powdered magnesium under dilute acid; and many other plans of action with powerful reducers have failed to yield analytical results comparable with those of the known methods. Hydrogen sulphide, dry or moist, and ammonium sulphide attack the halogen salts of silver with varying intensity, the chloride very easily, the bromide with less ease, and the iodide most difficultly —as might be predicted from a knowledge of the thermal values involved in the reactions. A current of hydrogen sulphide charged with ammonium sulphide effects the complete conversion of silver chloride to silver sulphide at a temperature below 200° C.; but we have never succeeded in securing absolutely complete conversion of the bromide to the sulphide by similar treatment even at much higher temperatures, and the iodide resists conversion more obstinately than the bromide. Nor have we been able to find conditions under which the chloride may be converted while the bromide and iodide remain unattacked. In a study of the conditions best adapted to the reduction of silver salts electrolytically we have obtained results which point to advantageous modifications of the methods heretofore known. We find that the treatment of the fused salts may be simplified, made more accurate, and extended to mixtures containing silver iodide.

In Kinnicutt's process the difficulties lie, first, in the impossibility of destroying the paper, upon which the silver salts have been collected and washed, without effecting some reduction of the salts; secondly, in the obstinacy with which the spongy silver holds the sulphuric acid during washing; and thirdly, in the tendency of the chlorine liberated when a chloride is present to attack the electrodes.

* Ber. Dtsch. chem. Ges., xxvii, 225. † Ibid., xiii, 500.

Upon the first point nothing need be said; the difficulty is obvious and well known. As to the second source of error, our experience shows that rapid washing is not sufficient to remove the sulphuric acid included in the reduced silver, even when excessive amounts of wash-water are used; but that a considerable time is indispensable for the escape of the acid from the silver to the wash-water by diffusion. In several cases we have found errors, ranging from a single milligram to six or seven, due to inclusion of the acid in residues which had been washed freely but rapidly, and which, even after ignition, yielded slowly hot water extracts which gave the test for a sulphate by barium chloride.

The results of some experiments made to test the effect of the halogens set free in electrolysis are shown in the accompanying table:

Electrolyte, 15 cm³ of H_2SO_4, (15 per cent) with the substance named.	Strength of current in ampères.	Time in hours.	Change in weight of the containing crucible.	Change in weight of wire electrode.	Connection of crucible.
			grm.	grm.	
1.7 grm. KI	0.46–0.25	24	0.0000	0.0000	Cathode.
1 " KBr	0.50–0.18	35	0.0000	0.0000	Cathode.
1 " KCl	0.48–0.18	26	0.0008–	0.0001–	Cathode.
0.5 " HCl	. . . .	. .	0.0009*–	0.0000	Cathode.
0.5 " HCl	0.3	48	0.0004–	0.0004+	Anode.

So it appears that, while neither bromine or iodine attacked the platinum perceptibly under the conditions of the experiments, though set free in abundance, an appreciable amount of the metal did dissolve under the action of chlorine. Moreover the solubility seems to depend chiefly upon the area of surface exposed and not upon the electric polarity. The metal dissolved was reprecipitated by the action of the current only in the experiment in which, by reversing the direction of the current and thus making the area of the anode large while that of the cathode was diminished, a corresponding increase of current density upon the cathode was brought about. It is

* Platinum tested for and found in solution.

obvious that under ordinary conditions of electrolytic reduction the solvent effect of the chlorine upon the platinum will naturally produce an apparent deficiency in the weight of silver reduced.

These sources of error in the electrolytic reduction of the fused silver salts we have endeavored to overcome. The danger of change in the constitution of the salts during preparation for weighing we avoid by collecting them upon asbestos in a perforated crucible instead of upon paper; but in order to secure perfect electrical conductivity throughout the mass of silver salts subsequently collected, dried, and weighed, we place a disc of perforated platinum foil upon the prepared felt of asbestos. In this way perfect electrical contact is obtained, though the rapidity of filtration is somewhat impaired. The disc also serves the useful purpose of preventing the disturbance of the felt by the gas evolved from the walls of the crucible in the electrolytic process.* When the silver salts have been collected, washed, dried and weighed, their fusion is effected by placing the capped crucible upon an anvil and directing the flame of a small blowpipe with care upon the mass from above. The anvil keeps the crucible cool and tends to prevent the soaking of the asbestos with the fused silver salts, which would be disadvantageous in the washing process which follows the reduction. A rubber band cut from rubber tubing of suitable diameter is adjusted so as to cover the junction between the cap and crucible and make a water-tight electrolytic cell. When the electrolytic reduction is finished the band and cap are removed, the crucible is put upon the pump, the liquid is drawn through and the precipitate washed in the usual manner.

It is obvious that the difficulty of washing out the sulphuric acid from the reduced silver may be avoided if it is possible to

* This device has been suggested by Puckner (Jour. Am. Chem. Soc., 1893, 710) for holding down the asbestos in an ordinary filtration, and is no doubt of value when suitable asbestos is not at hand. A fairly good asbestos properly prepared, and deposited upon a perforated surface in which the holes are sufficiently numerous — best, as numerous as can be — does not, however, tend to rise during a filtration so long as the suction pump is in action.

substitute for the sulphuric acid an electrolyte which, even if it were not easily removed by washing should be volatile at gentle heat without affecting the silver; and the danger arising from free chlorine may be obviated by taking care to have the chlorine absorbed by the electrolyte as soon as it is liberated. We find that twenty-five per cent alcohol containing a tenth of its weight of oxalic acid meets all the conditions for the electrolytic reductions of the mixed chloride and bromide of silver. Such a solution, while possessing sufficient conductivity, absorbs the free chlorine to such an extent that, as we have found experimentally, no perceptible solvent action takes place upon the platinum and nothing remains in the silver reduced under such a solution which is not volatile at gentle heat without affecting the weight of the silver.

In the test-experiments recorded in the accompanying table known amounts of silver chloride and bromide were precipitated, collected, washed, dried at 150°C., and weighed in the

AgCl taken.	AgBr taken.	Ag calculated.	Ag found.	Error.
grm.	grm.	grm.	grm.	grm.
1.0608	. . .	0.7985	0.7990	0.0005+
1.4380	. . .	1.0823	1.0823	0 0000
0.9908	. . .	0.7525	0.7522	0.0003–
. . .	0.9959	0.5721	0.5723	0.0002+
. . .	0.9079	0.5731	0.5732	0.0001+
1.0044	0.4988	1.0426	1.0422	0.0004–
0.4983	0.4966	0.6559	0.6568	0.0009+

filtering crucible provided as usual with a layer of asbestos which was in this case covered with the perforated platinum disc. The cap was put in place, the crucible set upon an anvil, and the salts fused with a blowpipe flame in the manner described. The rubber band was adjusted, the crucible nearly filled with the ten per cent solution of oxalic acid in twenty-five per cent alcohol, and the current passed in the usual manner, the crucible serving as the negative electrode. When the reduction was judged to be complete the band and cap were removed, the crucible set upon the pump, and filtration of the liquid and washing of the residue carried out as usual.

Finally the crucible, cap, and residue were ignited at a very low red heat and weighed. The entire treatment was repeated until the constant weight of the residue showed that the reduction was complete.

The manipulation of the method is very easy, and the results show that it is capable of yielding accurate results. The current ranged from 0.5 to 0.25 ampères, and for convenience the process was continued over night, though the reduction of amounts such as we treated is usually complete in six or seven hours.

Unfortunately this process which works so well with the mixture of chloride and bromide is not applicable to the reduction of silver iodide or to mixtures containing it. Experiment proved that the iodine set free in the electrolysis works over and over again upon the spongy silver constantly regenerating silver iodide to a greater or less degree. As the result of many attempts to destroy the liberated iodine without introducing anything objectionable into the solution we finally settled upon a mixture made by neutralizing two parts by volume of ordinary (40 per cent) acetic acid with ammonia, adding one part of ammonia, one part of alcohol, and one part of aldehyde (75 per cent). Such a solution we found to work very well on the whole, but as the reduction progresses it frequently happens that a deposit of white ammonium iodate forms upon the anode, which introduces too great resistance to the current. This deposit of iodate is, however, easily removed from the electrode by dipping it into hot water. Whenever the solution is so exhausted that free iodine begins to appear the liquid should be carefully decanted and replaced by fresh; and before the operation is ended the decanted solutions and the washings of the electrode should be filtered through the crucible, and the residue submitted again to the action of the current, to make it certain that loosened particles of silver or silver salt possibly poured off or removed on the electrode shall not be lost finally. The necessity of keeping the process under occasional supervision renders it undesirable to continue the action over night. In some cases of prolonged

action without attention we have noticed the formation of gummy carbonaceous matter which could not be subsequently removed without the application of a degree of heat which might endanger the platinum in contact with the reduced silver. Many of the experiments recorded in the following table were completed within seven hours with a current not exceeding 0.5 ampères:

AgCl taken.	AgBr taken.	AgI taken.	Ag calculated.	Ag found.	Error.
grm.	grm.	grm.	grm.	grm.	grm.
0.4779	. . .	. . .	0.3596	0.3591	0.0005–
0.6096	. . .	. . .	0.4588	0.4591	0.0003+
0.6774	. . .	. . .	0.5098	0.5099	0.0001+
. . .	0.9969	. . .	0.5727	0.5726	0.0001–
. . .	1.3703	. . .	0.7872	0.7875	0.0003+
. . .	. . .	1.0618	0.4878	0.4877	0.0001–
. . .	. . .	1.0621	0.4882	0.4875	0.0007–
. . .	. . .	1.0140	0.4661	0.4662	0.0001+
. . .	. . .	1.2012	0.5521	0.5530	0.0009+
. . .	. . .	1.5031	0.6910	0.6914	0.0004+
0.5035	0.4984	. . .	0.6653	0.6653	0.0000
1.0020	0.9998	. . .	1.3285	1.3283	0.0002–
0.4939	. . .	0.6561	0.6734	0.6733	0.0001–
. . .	0.5000	0.5304	0.5310	0.5316	0.0006+

These results show that the process affords an accurate reduction of the chloride, bromide, and iodide of silver and mixtures of these salts. When the problem concerns the reduction of the chloride and bromide only, we give the preference to the reduction in alcoholic oxalic acid as being the simpler process. The latter process we have also applied successfully on a larger scale to the recovery of the silver in chloride residues.

XLI

THE DETERMINATION OF SELENIOUS ACID BY POTASSIUM PERMANGANATE.

By F. A. GOOCH and C. F. CLEMONS.*

THE fact that sulphurous and tellurous acids may be oxidized quantitatively by a sufficient excess of potassium permanganate suggests naturally the application of the same general method to the determination of selenious acid. It is the object of this paper to record the results of experiments in this direction.

Brauner† found that in the action of the permanganate upon tellurous acid, whether in a solution acidified with sulphuric acid or made alkaline by caustic soda, the reduction of the permanganate does not proceed to the lowest degree of oxidation, the tellurous acid being unable to reduce the higher hydroxides of manganese which separate. In employing the reaction quantitatively it is necessary, therefore, to add the permanganate in distinct excess and then to destroy the surplus by means of standard oxalic acid added to the solution acidified with sulphuric acid, subsequently determining the excess of oxalic acid in the warmed solution by addition of more permanganate. The difference between the amount of permanganate actually used and that required to oxidize the known amount of oxalic acid introduced should naturally be the measure of the tellurous acid acted upon. Brauner found, however, an error in the process, by no means inconsiderable, due to the decomposition of the permanganate outside the main reaction. In a subsequent paper from this laboratory‡ it was shown that if the precaution is taken to restrict the

* From Am. Jour. Sci., 1, 51.

† Jour. Chem. Soc., lix, 238.

‡ Gooch and Danner, Am. Jour. Sci., xliv, 301. This volume, p. 145.

amount of sulphuric acid present in the solution when the permanganate acts the secondary decomposition involving loss of unutilized oxygen is kept within narrow bounds. In our work upon the oxidation of selenious acid we have followed the suggestions gained in the treatment of tellurous acid by Brauner's method.

The selenium dioxide which we employed was prepared from so-called pure selenium by dissolving the element in strong nitric acid, removing the nitric acid by evaporation, treating the aqueous solution with barium hydroxide to throw out any selenic acid formed in the oxidation, evaporating the solution to dryness, and subliming and re-subliming the residue in a current of dry air until the product was white. The oxide thus prepared was weighed out for individual experiments or was dissolved in a standard solution from which definite portions were drawn for use.

In the first series of experiments, the results of which are recorded in Table I, the selenium dioxide was dissolved in 100 cm^3 of water, 10 cm^3 of sulphuric acid of half-strength were added, an approximately decinormal standardized solution of potassium permanganate was added until the characteristic color predominated over that of the brown hydroxide deposited during the oxidation, oxalic acid in solution of known strength was introduced until the excess of permanganate had been destroyed and the insoluble hydroxide dissolved, and, finally, after heating the solution to about 80° C., more of the permanganate was added to the color reaction. The final volume varied from 250 cm^3 to 350 cm^3, so that the sulphuric acid (absolute) present varied from about five per cent at the start to from one and a half to two per cent at the end.

When the permanganate is first introduced into the acidified solution the color vanishes, leaving a clear colorless liquid, but as more is added the solution becomes yellow and deepens gradually in color to a reddish brown, until turbidity due to the deposition of a brown hydroxide of manganese ensues, and finally the characteristic color of the permanganate is plainly distinguishable. The exact point at which precipitation of

the manganic hydroxide begins depends upon the dilution, acidity, and temperature of the solution. In experiments (1) and (2), the permanganate was added to the cold solution at the first, but the liquid was heated after the addition of oxalic acid and before the final titration with the permanganate. The remaining determinations of the series were made in solutions kept hot throughout.

TABLE I.

[Se = 79.1, O = 16.]

Exp.	SeO_2 taken.	Oxygen equivalent of permanganate used.	Oxygen equivalent of oxalic acid used.	SeO_2 found.	Error.
	grm.	grm.	grm.	grm.	grm.
(1)	0.1000	0.03026	0.01571	0.1010	0.0010+
(2)	0.1002	0.03038	0.01578	0.1014	0.0012+
(3)	0.0997	0.02634	0.01182	0.1008	0.0011+
(4)	0.0999	0.02568	0.01122	0.1004	0.0005+
(5)	0.1000	0.02536	0.01077	0.1012	0.0012+
(6)	0.1000	0.03226	0.01765	0.1015	0.0015+
(7)	0.1001	0.04455	0.02992	1.1016	0.0015+
(8)	0.2001	0.05448	0.02543	0.2018	0.0017+
(9)	0.1997	0.05219	0.02318	0.2014	0.0017+
(10)	0.1997	0.05215	0.02318	0.2011	0.0014+
(11)	0.5178	0.13215	0.05721	0.5203	0.0025+
(12)	0.5197	0.14105	0.06541	0.5252	0.0055+

An examination of these results develops the fact that the action proceeds regularly in the main under the conditions of experimentation, but that there is an apparent waste of permanganate in the process. It was observed that the addition of a little permanganate beyond the exact amount necessary to produce the end-reaction occasioned the precipitation of manganese hydroxide, evidently, according to Guyard's reaction, by interaction between the permanganate and the manganous sulphate present. Plainly the amount of sulphuric acid present, which we kept purposely low to obviate the spontaneous decomposition of the permanganate, was not sufficient to prevent the ultimate formation of the hydroxide at the temperature of action. The natural inference is that the difficulty in the determinations may have been due rather to an interference with the color reaction at the end of the

oxidation process, due to the incipient tendency of the permanganate to act upon the manganous salt, than to direct loss of oxygen from the permanganate. If this is true, the obvious and simple remedy should be found in effecting the oxidation of the oxalic acid at the end of the process at a temperature so low that the inclination of the permanganate and manganous sulphate to interact shall be diminished. Table II contains the record of experiments in which this precaution was taken. The entire process of oxidation, which was otherwise similar to that of the previous experiments, was brought about between the temperature of 75° C. at the beginning and 50° C., or even a little less, at the end. The end-reaction was in every case sharp and the final color was permanent for several minutes at the least.

TABLE II.

Exp.	SeO_2 taken.	Oxygen equivalent to permanganate used.	Oxygen equivalent to oxalic acid used.	SeO_2 found.	Error.
	grm.	grm.	grm.	grm.	grm.
(13)	0.1000	0.03506	0.02065	0.1001	0.0001+
(14)	0.1000	0.03519	0.02073	0.1004	0.0004+
(15)	0.1000	0.03706	0.02255	0.1007	0.0007+
(16)	0.1000	0.03853	0.02422	0.0994	0.0006−
(17)	0.1000	0.03512	0.02065	0.1005	0.0005+
(18)	0.2000	0.06124	0.03256	0.1994	0.0006−
(19)	0.2011	0.06069	0.03177	0.2008	0.0003−
(20)	0.2004	0.06072	0.03177	0.2010	0.0006+
(21)	0.2020	0.06083	0.03185	0.2012	0.0008−
(22)	0.2038	0.06106	0.03185	0.2028	0.0010−

These results are evidently an improvement upon those of the first series of experiments, and are fairly satisfactory so far as concerns the estimation of the amounts of selenium dioxide discussed. The determination of large amounts of selenious acid by this method is somewhat less advantageous than it would be if the reduction of the permanganate proceeded farther in the first action. One hundred cubic centimeters of a standard solution is as much as can be conveniently handled in a single process of titration, and that volume of decinormal permanganate (which is about as

strong as the standard solution should be when accurate work is expected) is capable of oxidizing about 0.25 grm. of selenium dioxide.

The process which we recommend consists, in brief, in the addition of standard potassium permanganate to the solution of selenious acid containing not more than five per cent of its volume of strong sulphuric acid, the introduction of standard oxalic acid until the liquid clears, and the titration of the excess of oxalic acid by permanganate, at a temperature not much exceeding 50° or 60° C. The permanganate and the oxalic acid should be standardized under similar conditions of acidity and temperature, and for a standard of final reference we prefer pure crystallized ammonium oxalate.

We have made experiments in which the initial oxidation of the selenious acid was made in alkaline solution, but inasmuch as the amount of permanganate required for the oxidation is about three times as great as that needed in the acid solution the treatment in alkaline solution is practically inferior.

XLII

THE PRECIPITATION AND GRAVIMETRIC DETERMINATION OF CARBON DIOXIDE.

By F. A. GOOCH and I. K. PHELPS.*

THE method upon which reliance is most confidently placed for the determination of carbon dioxide in solid carbonates, involving as it does the liberation of that gas by the action of a strong acid and its absorption in weighed potash-bulbs, demands as conditions of the attainment of good results the careful observance of precautions and the expenditure of much time and attention. In the method described below we have sought to secure equal accuracy with greater economy of time and care. Our plan is to effect the rapid absorption of the carbon dioxide, evolved by the action of acids upon carbonates, in barium hydroxide contained in a specially devised apparatus, to filter and wash the precipitated barium carbonate under a protecting layer of xylene, to dissolve in hydrochloric acid the washed carbonate upon the filter or adhering to the receiver, to convert the barium chloride thus obtained into the form of the sulphate, and from the weight of the last to calculate the carbon dioxide originally liberated by acid from the carbonate.

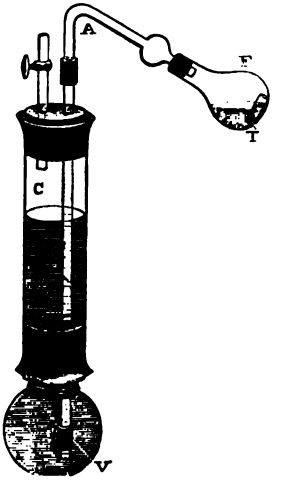


FIG. 10.

* From Am. Jour. Sci., I, 101.

The apparatus which we use, and which is shown in the figure, consists of a flask for the evolution of the carbon dioxide, properly connected with a receiver in which the gas is retained until absorption is perfect. It is a form of a similar device employed by one of us* for the absorption of ammonia in hydrochloric acid and the complete retention of the ammonium salt thus formed, but so modified as to avoid the danger of diffusion of carbon dioxide through the rubber balloon — a source of error which we have found by experiment to be considerable when large amounts of the gas are handled.

The evolution flask (F) has a capacity of about 50 cm^3, and is fitted with a rubber stopper through which passes a tube (A) wide enough (about 0.7 cm. in interior diameter) to prevent the formation of bubbles, and expanded just above the stopper to a small bulb. The absorption cylinder consists of a wide glass tube (C), fitted at either end with a rubber stopper. The stopper at the lower end of the cylinder, placed vertically, carries a short tube, about 1.5 cm. in diameter, to which is secured a smaller rubber balloon. The cylinder and balloon together hold about 100 cm^3. The upper stopper is perforated with two holes, through one of which passes the tube of a glass stop-cock, while through the other hole passes a long tube reaching to the interior of the balloon and provided with a valve (V) — preferably a modified Bunsen valve, of the pattern recently devised by Kreider and described on page 307.

In using this apparatus a saturated solution of barium hydroxide (which is made hot, filtered into a siphon-bottle, and preserved from atmospheric action by a floating layer of kerosene) is introduced by pressure upon the air in the siphon-bottle or by suction applied to the stop-cock of the cylinder. Such a solution contains about five per cent of its weight of the hydroxide, and we find it best to use in every case an amount at least a fourth in excess of the quantity theoretically required to absorb the carbon dioxide, and to fill

* Am. Chem. Jour., i, 450.

the cylinder and balloon nearly full of liquid. The carbonate is weighed, introduced into the flask, and washed down with fifteen or twenty cubic centimeters of boiled water, which is protected in the wash-bottle from carbon dioxide in the breath by a balloon attached to the inlet tube. A small tube holding enough hydrochloric acid to effect the decomposition of the carbonate to be analyzed, is placed in upright position in the evolution flask. The stopper is inserted in the flask and connections are made as shown in the figure, the little tube containing the acid is overturned by inclining the flask, the acid mixes with the water and effervescence begins. Heat is applied and the liquid in the flask is boiled until that in the cylinder is heated by the steam nearly to the boiling point, in order that the precipitated barium carbonate may become as granular as possible. The carbon dioxide evolved and the air in the flask are transferred in the process to the absorption cylinder, the valve serving to prevent the back-flow of the liquid while the balloon expands to give room to the air and condensed steam. When the boiling is done the flask and tube are disconnected at the rubber joint, the cylinder is shaken to insure the absorption of the carbon dioxide, and the liquid carrying the greater part of the precipitate is transferred through the stop-cock to a filter carefully fitted to its funnel, moistened with water and containing about 5 cm^3 of xylene, which we found to be preferable to benzene, kerosene, or amyl alcohol, the function of which is to rise to the surface when the aqueous solution is added so as to protect the barium hydroxide from the action of the carbon dioxide of the air. By manipulating the balloon and the stop-cock (to which a little funnel may be attached by a piece of rubber tubing for convenience in introducing wash-water) the cylinder may be emptied and washed out with hot boiled water, though, of course, a very considerable portion of the precipitate remains adhering to the walls of the absorption apparatus.

We prefer to prepare the filter for use with the suction pump, but in the early stages of filtration and washing very

little suction should be applied. When the barium hydroxide has been nearly washed out of the precipitate, the xylene is dissolved in a little hot alcohol, the suction is applied and the washing is completed with hot water. The emulsion of xylene and water found in the filtrate is readily cleared up by alcohol. Finally, the barium carbonate in the absorption apparatus and upon the filter is dissolved in hydrochloric acid and precipitated in hot solution by sulphuric acid, the resulting barium sulphate is filtered, washed and ignited upon asbestos in a perforated crucible, and from its weight the carbon dioxide which originally precipitated the barium, now in the form of the sulphate, is calculated. The results of a series of determinations made in this manner are recorded in the following table:

[Ba = 137.43, S = 82.06, O = 16, C = 12.]

$CaCO_3$ taken.	$BaSO_4$ found.	CO_2 actually present.	CO_2 calculated.	Error in CO_2.
grm.	grm.	grm.	grm.	grm.
0.0500	0.1180	0.0220	0.0222	0.0002+
0.0500	0.1183	0.0220	0.0223	0.0003+
0.1000	0.2329	0.0440	0.0439	0.0001−
0.1000	0.2347	0.0440	0.0442	0.0002+
0.2000	0.4660	0.0880	0.0878	0.0002−
0.2000	0.4653	0.0880	0.0876	0.0004−
0.5000	1.1650	0.2200	0.2196	0.0004−
0.5000	1.1657	0.2200	0.2197	0.0003−
1.0000	2.3323	0.4400	0.4396	0.0004−
1.0000	2.3309	0.4400	0.4394	0.0006−

Various modifications of method and manipulation were put to the test of experiment, but the process which we have described has proved on the whole the most satisfactory. It is fairly rapid and accurate.

The valve thus lubricated with glycerin when used as a protection in an ammonia wash-bottle, will prevent absolutely the access of ammonia to the mouth, and if made according to the directions will act with very little pressure. Placed in the connection between the vacuum flask and water pump ordinarily used in filtration, it has been found a valuable check on the valve of the pump, and when the latter was impotent this device prevented any water being drawn into the filtrate. In a process soon to be published, in which a partial vacuum is used, this valve holds the vacuum in continual readiness and adds greatly to the convenience of the process.

Force Pump. — By adjusting two of the valves just described to the opposite extremities of a T-tube, with the horizontal limb enlarged or sealed to a larger tube so as to permit the attachment of a large and stout piece of rubber tubing closed at one end, as shown in Fig. 13, a convenient and powerful little force pump is obtained. A small bore, stout T-tube is cut off short at the two ends at right angles to one another: to one is sealed a tube just large enough to permit the insertion of a valve; to the other, a large tapering tube, slightly lipped so as to hold a piece of rubber tubing firmly and allow of tying the latter if necessary. Of the third end of the tube, a valve like that shown in Fig. 12 is made. The compressing rubber should not be of greater length than the hand is able to cover completely and may be closed with a glass stopper selected to fit tightly. Providing the space through the T-part is kept at a minimum compared with that of the compressing rubber, rapid pumping will be found possible and the power limited only by the strength of the user's grip. A column of water was quickly raised and forced from the top of a tube sixteen feet in length. The apparatus will be found convenient in the absence of a regular pump and can be quickly constructed of materials always at hand. Originally it was made, in about fifteen minutes, of a T-tube to which the necessary enlarge-

FIG. 13.

ments were connected by rubber tubing and the unused space filled by a glass rod. The valves may be inserted directly into the ends of the compressing rubber, but the form shown in the figure will be found more serviceable. By attaching the lower end to a tapering tube as shown, the pump is easily inserted into any sized perforation of a stopper and adds greatly to its convenience.

The pump has been found serviceable in various applications. For filling burettes it will be found more advantageous than the siphon plan. The standard solution bottles are fitted with two-holed stoppers, from one of which a tube of sufficient length is bent so as to reach into the burette. The pump can be applied to various bottles by the adapter shown in the figure and the solutions forced into the burettes. To prevent any evaporation in the tube a glass stop-cock may be inserted. On several occasions it has been applied to a Kipp generator in which higher pressure was momentarily required. In various other ways it has been found a useful piece of apparatus.

XLIV

THE REDUCTION OF THE ACIDS OF SELENIUM BY HYDRIODIC ACID.

By F. A. GOOCH and W. G. REYNOLDS.*

A METHOD for the iodometric determination of selenious acid has been recently announced by Muthmann and Schaefer† which is based upon the reduction of selenious acid by hydriodic acid and the direct titration of the iodine thus liberated. To determine the selenious acid it is only necessary to add it in solution to an acidulated solution of potassium iodide, when iodine and selenium are both set free in elementary form, the former being directly determinable by titration with sodium thiosulphate after addition of starch. The difficulty in the process is said to be the uncertainty as to the exact point in the titration at which the starch blue disappears from the liquid in which the finely divided and opalescent selenium is held in suspension. For this reason the process is recommended for use only when great accuracy is not essential.

Evidently if the reaction between the acidulated iodide and selenious acid is single and complete, the process should be capable of improvement by removing the selenium before the titration is attempted. This we have succeeded in doing without difficulty. We find the most convient and rapid way to remove the finely divided selenium is to filter the liquid containing it by means of the vacuum pump upon a thick felt of asbestos in a perforated crucible or cone of large filtering surface. With a properly prepared filter of this description there is no difficulty in separating the selenium in

* From Am. Jour. Sci., 1, 254.

† Ber. Dtsch. chem. Ges., xxvi, 1008.

a very few moments so completely that it is possible to determine the iodide remaining dissolved in the excess of potassium iodide with all the accuracy characteristic of this most exact of titration processes. We find, however, that when the difficulty of determining the end-reaction in the titration of the iodine by the thiosulphate is overcome, it becomes apparent that the reaction upon which Muthmann and Schaefer depend is not perfect. Either the reduction of the selenious acid to selenium is not complete, or else the iodine remains in combination to a slight extent with the selenium and so fails to appear in the filtrate. This is evident from the results of the experiments of Table I, in which the selenious acid and potassium iodide acidulated with hydrochloric acid were brought together, the liquid thrown upon the asbestos filter, the selenium washed until free from soluble iodine, and the filtrate containing the iodine treated as usual with sodium thiosulphate in presence of starch. The details of treatment are described sufficiently in the table. The selenium dioxide was prepared for the work from the so-called pure elementary selenium by dissolving it in strong nitric acid, evaporating off the excess of the last, treating the solution of the residue in water with barium hydroxide, filtering to remove selenic acid formed in the oxidation and traces of sulphuric acid possibly present as an impurity, recovering the selenium dioxide by evaporation, and purifying it by subliming and re-subliming it in a current of dry air until it was clean and white.

TABLE I.

SeO_2 taken.	KI used.	HCl used. (Sp. gr. 1.20).	Volume before filtering.	SeO_2 found.	Error.
grm.	grm.	cm^3	cm^3	grm.	grm.
0.0499	1	5	100	0.0479	0.0020–
0.0499	1	5	100	0.0477	0.0022–
0.2035	3	5	100	0.1896	0.0139–

From these figures it is plain that iodine was not found in the filtrate in amount corresponding to the selenium dioxide

present. In the following experiments of Table II. an excess of the thiosulphate was added before filtering off the selenium so that there should be every opportunity for the iodine and thiosulphate to interact before the removal of the selenium. In two experiments the proportion of hydrochloric acid was increased tenfold for the purpose of seeing whether the presence of a large amount of free acid influences the result.

TABLE II.

SeO_2 taken.	KI used.	HCl used. (Sp. gr. 1.20).	Volume before filtering.	SeO_2 found.	Error.
grm.	grm.	cm^3	cm^3	grm.	grm.
0.0499	1	5	100	0.0489	0.0010–
0.0499	1	8	100	0.0485	0.0014–
0.0499	1	50	100	0.0489	0.0010–
0.0499	1	50	100	0.0488	0.0011–
0.2006	3	5	100	0.1925	0.0081–
0.2030	3	5	100	0.1945	0.0085–

These results show improvement over those obtained when filtration is made before acting with the thiosulphate, but it is obvious that the presence of a large proportion of free hydrochloric acid is without effect upon the reaction, and that the iodine set free and measured is still deficient in proportion to the amount of selenium dioxide present. Plainly the reduction of the selenium dioxide is incomplete, or else there is formed between the selenium and iodine a combination, such as was noticed by Hautefeuille * in the interaction of iodine upon hydrogen selenide. In either case it should be possible to push the reaction farther toward completion by submitting the mixture of selenious acid, potassium iodide, and hydrochloric acid to distillation. We have used for this purpose an apparatus employed and described in connection with previous similar work in this laboratory. The distillation flask is a Voit gas-washing flask, and this is sealed to the inlet tube of a Drexel wash-bottle used as a receiver, to the outlet tube of which is sealed a

* Compt. rend., lxviii, 1554.

Will and Varrentrapp absorption apparatus to serve as a trap. The mixture to be distilled was introduced into the flask, a solution of 3 grm. of potassium iodide in 100 cm^3 of water was put into the receiver and trap and during the distillation a slow current of carbon dioxide was passed through the apparatus to keep the boiling regular. Naturally the acidified solution of the iodide in the flask retains with great tenacity traces of dissolved iodine, so that, in order to determine all the iodine liberated in the reaction, the residue in the flask as well as the distillate in the receiver and trap was titrated in the usual way with sodium thiosulphate. The details of treatment and the results are recorded in Table III.

TABLE III.

SeO_2 taken.	KI in flask.	HCl in flask. (Sp. gr. 1.20).	Total volume boiled.	Time in minutes.	SeO_2 found.	Error.
grm.	grm.	cm^3	cm^3		grm.	grm.
0.0499	1	5	60	5	0.0497	0.0002—
0.0499	1	5	60	5	0.0497	0.0002—
0.0499	1	5	60	10	0.0496	0.0003—
0.2000	3	5	60	10	0.1995	0.0005—
0.2000	3	5	60	10	0.1991	0.0009—
0.2023	3	5	60	10	0.2018	0.0005—
0.5018	3	5	60	10	0.4635	0.0383—

These results are all fairly good, though all a little deficient, for amounts of selenium dioxide up to 0.2 grm.; but when the amount of the dioxide reaches 0.5 grm. the iodine found in the distillate and in solution in the residue falls far below the theory based upon the assumption that the products are selenium, iodine, and water. The selenium in the residue was left after the boiling in fine dense crystalline condition in the experiments with the smaller amounts, so that it did not interfere with the titration of the free iodine; but in the last experiment, in which approximately 0.5 gram of the dioxide was treated, the selenium remained in pasty form adhering to the flask. Subsequent examination proved that the pasty selenium held iodine, which was liberated slowly

to water and more rapidly to an aqueous solution of potassium iodide.

The largest errors have been found (excepting that of the last experiment from the discussion) when the free iodine was filtered off from the reduced selenium; better results were obtained when the precipitated selenium was first treated with the thiosulphate before filtering; and in the distillation process the best approximations are made to true indications. It is obvious that as the proportion of selenium and iodine increase, the tendency to form a combination is more manifest. The error thus introduced in the determination of the selenium dioxide by the distillation process is allowable up to the limit of 0.2 grm.

Potassium iodide in hydrochloric acid acts much less readily upon selenic acid than upon selenious acid. When the hydrochloric acid is present in small proportions in the mixture of selenic acid and the iodide the reduction is very imperfect, but it tends to approach completion as the strength of hydrochloric acid is increased.

It is obvious, in the light of the previous experiments with selenious acid, that it is unreasonable to expect the full liberation of iodine in the action of selenic acid upon the iodine when the free iodine is not removed from the sphere of action as it is liberated. In the distillation process the case is otherwise, and there is no reason to anticipate that

TABLE IV.

SeO_3 taken.	KI in flask.	HCl flask. (Sp. gr. 1.20).	Total volume boiled.	Time in minutes.	SeO_3 found.	Error.
grm.	grm.	cm^3	cm^3		grm.	grm.
0.0593	1	5	60	5	0.0593	0.0000
0.0593	1	5	60	5	0.0591	0.0002−
0.0593	3	5	60	10	0.0596	0.0003+
0.1779	3	5	60	10	0.1769	0.0010−
0.1779	3	5	60	10	0.1780	0.0001+
0.1779	3	5	60	10	0.1764	0.0015−

the determination of selenic acid should present greater difficulty than is encountered in treating selenious acid under

similar circumstances. The experiments of Table IV, in which selenic acid (obtained by oxidizing known amounts of selenium dioxide by means of potassium permanganate in the manner described in a previous paper from this laboratory) * is treated according to the distillation method outlined above for the determination of selenious acid, show that this expectation is realized, and that the analytical results are fairly good.

In conclusion, it is plain that while the simple contact of solutions of selenious acid or selenic acid and potassium iodide acidified with hydrochloric acid does not determine the liberation of the full amount of iodine which would be expected if selenium, iodine, and water were the sole products of action, it is possible to bring about such action with a close approximation to completeness, when the amounts of selenium present are not too large, by submitting such mixtures to distillation. We prefer, in applying the reaction to analytical purposes, to work with the apparatus and under the conditions described — treating, preferably, not more than 0.2 grm. of the selenium oxide, using from 1 grm. to 3 grm. of potassium iodide in the distilling-flask with 5 cm^3 of strong hydrochloric acid in a total volume of 60 cm^3 and continuing to boil for ten minutes.

* Gooch and Clemons, Am. Jour. Sci., l, 51. This volume, p. 297.

XLV

THE QUANTITATIVE DETERMINATION OF PERCHLORATES.

By D. ALBERT KREIDER.*

THE method usually employed for the quantitative determination of perchlorates, by igniting to the chloride and weighing the halogen as the silver salt, is indirect and subject to error, especially, as my experience proved, where the free acid is to be determined and where, consequently, an alkali which is apt to contain chloride is used to form the salt for the ignition. To purify the salt for this method only adds to the complication, and therefore a more satisfactory process was sought. In a recent article† from this laboratory, a method for the detection of alkaline perchlorates associated with chlorides, chlorates and nitrates were detailed, with mention of certain efforts towards a quantitative determination. As throwing light upon the peculiar properties of perchlorates, and as an introduction to the satisfactory method which I have finally developed, some of the results of these earlier efforts will here be given.

In studying the properties of perchloric acid in the form of its potassium salt, we found that when treated with potassium iodide in the presence of boiling phosphoric acid, no reduction of the perchlorate is effected; unless indeed, the boiling be continued till the temperature rises to 215° to 220° C., where the meta-phosphoric acid begins to form. But when the meta-phosphoric acid (made by heating the syrupy ortho-acid to 360° C.) is directly applied in the presence of potassium iodide and kept at a temperature of about 200° C., iodine is

* From Am. Jour. Sci., 1, 287.

† Gooch and Kreider, Am. Jour. Sci., xlviii, 38. This volume, p. 246.

copiously evolved. To test this reaction quantitatively a number of experiments were made in an apparatus consisting of a retort, into the tubulature of which a glass tube was carefully ground and prolonged so as to reach to the bottom of the bulb and serve for the passage of a current of carbon dioxide, used to expel the air and carry the iodine into the receiver. The neck of the retort was bent so as to reach to the bottom of an Erlenmeyer receiving vessel, containing a solution of potassium iodide, which was trapped by a side-necked test tube. After introducing the perchlorate with the iodide and meta-phosphoric acid, all air was expelled by carbon dioxide and heat applied. The iodine collected in the receiver was titrated with decinormal thiosulphate, from which the perchlorate was calculated.

Table I gives the results of several experiments performed in this way, which prove that even with a large excess of potassium iodide the perchlorate is so slowly reduced that the hydriodic acid escapes before the reduction is completed. In order to delay the distillation of hydriodic acid until the perchlorate had been completely reduced, the potassium iodide of experiment (3) was introduced in a short tube sealed at one end, so that the meta-phosphoric acid could attack it only slowly, and the heat quickly raised to about 300° C., but evidently without advantage. In experiment (4) the iodide was introduced in the same way, but the heat was applied gradually and more moderately, with considerably improved results.

TABLE I.

Exp.	$KClO_4$ taken.	$HOPO_3$ used.	KI used.	$KClO_4$ found.	Error.
	grm.	cm^3	grm.	grm.	grm.
(1)	0.1000	15	5	0.0741	0.0259–
(2)	0.1000	17	10	0.0844	0.0156–
(3)	0.1000	15	5	0.0364	0.0636–
(4)	0.1000	15	5	0.0977	0.0023–

A complete reduction of the perchlorate evidently necessitated the means of introducing the iodide in sufficient quantity and at will.

For this purpose the tube serving for the introduction of carbon dioxide was enlarged so as to hold the iodide, which could then be added to the solution at any time by a manipulation of the rubber conducting-tube for carbon dioxide, which would draw the acid up to the iodide and, retreating, would carry back an easily regulated quantity of the latter.

TABLE II.

Exp.	$KClO_4$ taken.	KI used.	$KClO_4$ found.	Error.
	grm.	grm.	grm.	grm.
(5)	0.1000	5	0.0984	0.0016–
(6)	0.1000	3	0.0924	0.0076–
(7)	0.0500	2	0.0508	0.0008+
(8)	0.0500	2	0.0479	0.0021–
(9)	0.1000	7	0.0977	0.0023–
(10)	0.1000	3	0.0925	0.0075–
(11)	0.1000	3	0.0999	0.0001–
(12)	0.1000	2	0.0994	0.0006–
(13)	0.1000	4	0.0966	0.0034–

Table II gives a number of results obtained in this way. Experiments (10), (11), and (12) differed from the others only in the employment of a bulb pipette instead of the retort, one end being bent so as to reach to the receiver and the other cut off rather short with a tube ground into it, serving the same purpose of conducting carbon dioxide and holding potassium iodide, the greater inclination of the potassium iodide tube made possible by this change appearing to offer advantages for the more gradual and regular introduction of the iodide. The amount of meta-phosphoric acid used was in all cases 15 cm^3. In experiment (13) heat was applied by means of a bath kept at 230°.

While several of these determinations gave only admissible errors, the irregularity of the remainder and the uncertainty in striking just the proper conditions for good results, proved the method worthless at least in that shape.

The experiments of Table III record the results of adding the acid drop by drop to an intimate mixture of the powdered perchlorate and iodide kept hot.

TABLE III.

Exp.	$KClO_4$ taken.	KI taken.	$KClO_4$ found.	Error.
	grm.	grm.	grm.	grm.
(14)	0.1000	4	0.1036	0.0036+
(15)	0.0500	2	0.0502	0.0002+
(16)	0.0500	3	0.0515	0.0015+

The high results of this table doubtless point to the dissociation of hydriodic acid or to the partial reduction of the meta-phosphoric acid in the temperature, which would naturally rise higher where so small an amount of liquid was present. But when the meta-phosphoric acid was there in greater amount the distillation of the hydriodic acid before the complete reduction of the perchlorate could not be prevented.

An ordinary mixture having thus been found insufficient to hold the hydriodic acid to the reduction of perchlorates, a search for some compound in which the perchlorate could be fused with an excess of potassium iodide and the mixture thus obtained subjected to the action of meta-phosphoric acid resulted in the employment of zinc chloride. Anhydrous zinc chloride was found to fuse at about 200° C. The perchlorate and iodide could be added to this fusion and the whole melted, thoroughly diffused, and cooled without any evolution of iodine. This mass, when treated with meta-phosphoric acid in the apparatus previously employed, melted gradually with a copious evolution of iodine. Table IV shows the quantitative action. The amount of zinc chloride used was roughly taken about equal to that of the iodide.

TABLE IV.

Exp.	$KClO_4$ taken.	KI taken.	$KClO_4$ found.	Error.
	grm.	grm.	grm.	grm.
(17)	0.0500	5	0.0552	0.0052+
(18)	0.0000	5	0.0044	0.0044+
(19)	0.0000	4	0.0057	0.0057+

In (19) a mixture of cadmium iodide and potassium iodide taken in the proportion of their molecular weights was substi-

tuted for the zinc chloride. The known salt corresponding to the formula $CdI_2 . 2KI + 2H_2O$ was not so convenient because of its high melting point, 230° C.; but when the two iodides are taken in the proportion of their molecular weights, the mixture fuses at about 200° C. Although this mass after fusion was more easily soluble than the zinc residue, the blank determination revealed a source of error equally disparaging.

Gaseous hydriodic acid passed into a mixture of the perchlorate and meta-phosphoric acid at a temperature between 200° and 300° C was markedly less effective than the generation of the acid on the spot; and the distilling of the perchloric acid by meta-phosphoric acid into a receiver of potassium iodide yielded only a trifling amount of iodine, while the passage of hydriodic acid over the fusing perchlorate in a short combustion tube was precluded by the high melting point of the perchlorate endangering the dissociation of the halogen.

The invariably high results obtained by the use of meta-phosphoric acid in all those experiments in which there was a reasonable assurance that the hydriodic acid was held till the perchlorate was completely broken up, — experiments (13), (14), (15), (17), (18), and (19), — indicated either a dissociation of hydriodic acid or a partial reduction of the meta-phosphoric acid. Of the latter cause there were some grounds for suspicion, but as its determination led too far from the object of the investigation, the use of phosphoric acid was abandoned. So far as our experience extended there remained then nothing among the reagents of the wet methods which was sufficiently active and stable enough to warrant its application. Fusion alone seemed capable of extracting the oxygen from the perchlorate. A number of preliminary tests were therefore made on certain salts of the halogens, in the hope of finding one which would be acted upon by the oxygen of the perchlorate with the liberation of the halogen, which latter could be collected in a receiver of potassium iodide and titrated with thiosulphate.

The double chloride of aluminum and sodium, $Al_2Cl_6 . 2NaCl$, melts at about 200° C., and was in other respects desirable.

When fused with potassium perchlorate, chlorine was copiously evolved. The action of air on the fusion also liberated chlorine; but blank determinations in an atmosphere of carbon dioxide proved that under these conditions not a trace of chlorine was evolved. The apparatus employed for a quantitative test of this reaction on perchlorates consisted of a small distilling flask of about 20 cm^3 capacity, into the tubulature of which was ground a piece of glass tubing reaching well into the bulb and serving for the passage of carbon dioxide. The side neck was sealed to one of two connected Will and Varrentrapp absorption bulbs containing a solution of potassium iodide to receive the chlorine. After weighing the perchlorate into the flask and adding a sufficient amount of the powdered double chloride, all air was expelled by carbon dioxide and heat applied till the fused mass was raised considerably above the melting point and kept there for some time. Table V contains the results of a number of experiments performed in this way.

TABLE V.

Exp.	$KClO_4$ taken.	$KClO_4$ found.	Error.
	grm.	grm.	grm.
(20)	0.0500	0.0488	0.0062–
(21)	0.0500	0.0482	0.0018–
(22)	0.0500	0.0460	0.0040–
(23)	0.1193	0.1175	0.0018–
(24)	0.1039	0.1018	0.0021–
(25)	0.0500	0.0477	0.0023–
(26)	0.1003	0.0946	0.0057–

These results came so close to being quantitative that a little help in the form of free acid seemed all that would be necessary to complete the reaction. But the addition of meta-phosphoric acid to the cooled mass after the fusion in (22) gave no additional evolution of iodine. In (25) gaseous hydrochloric acid was passed in with the carbon dioxide in the hope of meeting the deficiency, but was evidently no improvement. One test in which meta-phosphoric acid was added to the fusion, resulted in such a violent evolution of

hydrochloric acid that the whole contents of the flask was forced into the receivers.

The results obtained by substituting (*a*) cadmium iodide and (*b*) anhydrous zinc chloride for the double chloride of aluminum and sodium are recorded in Table VI. In (27) (28) and (29) cadmium iodide was used and the iodine obtained by treating the cooled mass with dilute sulphuric acid (1 : 6) and potassium iodide for the reduction of cadmium oxide in each case added to that of the receivers. In (30) and (31), zinc chloride was employed, but no additional iodine was obtained by treatment with sulphuric acid and potassium iodide.

TABLE VI.

Exp.	$KClO_4$ taken.	$KClO_4$ found.	Error.
	grm.	grm.	grm.
(27)	0.1000	0.0745	0.0255–
(28)	0.1000	0.0693	0.0307–
(29)	0.1000	0.0679	0.0321–
(30)	0.1000	0.0245	0.0755–
(31)	0.1653	0.1156	0.0497–

In (31) manganous chloride was mixed with the zinc chloride in the proportion of 2 : 1 in the hope of strengthening the reducing action. The black color of the fusion revealed the formation of manganese dioxide, the equivalent of which in iodine was obtained by dissolving the cooled mass in water, adding dilute sulphuric acid and a known amount of ammonium oxalate, titrating the residual oxalate with permanganate solution and calculating the difference into iodine which was added to that obtained by titrating the contents of the receivers. This addition of manganous chloride to the fusion of the double chloride of aluminum and sodium was forestalled by the necessity of subsequent solution of the fused mass, which contained an impurity in the form of ferric chloride, which of course in the presence of hydriodic acid would be reduced with evolution of iodine.

It was evident from all these results, as well as those obtained by use of other salts not necessary here to record,

that fusion with salts of the halogens would not suffice for the complete reduction of perchlorates, or at least would not quantitatively register the result in the halogen liberated. The well known reaction of the oxidation of chromic oxide by fusion with alkaline carbonates was also applied. A combustion tube was used for the fusion, sealed at one end and, after the insertion of chromic oxide with a mixture of sodium and potassium carbonate, constricted at the other end so as to admit a small tube by which carbon dioxide could be entered to expel all air. A blank determination gave no chromate. When 0.1 grm. potassium perchlorate was mixed with an excess of chromic oxide and alkaline carbonate and carefully fused from the top and kept in a state of fusion throughout its length in an atmosphere of carbon dioxide, the fusion subsequently dissolved in water and the chromic oxide removed by filtration, an amount of chromate was obtained on titration equivalent to only 0.0347 grms. of potassium perchlorate.

Powerful as were the various reducing agents employed for the decomposition of perchlorates, they were all successfully resisted, even at the highest permissible temperatures; and if anything is proved by the results of the experiments above recorded, it is that perchloric acid is, in combination, one of the most powerful and stable acids known. Certainly nothing short of high temperatures is capable of overcoming the remarkable affinity by which the oxygen of this acid is held by its salts. At about 400° C. the potassium salt fuses with evolution of oxygen, and as a last resort an attempt was made to have the oxygen thus obtained act on hydriodic acid by intervention of nitric oxide. It was the application of this principle that led to the final method, which, both as to manipulation and results, leaves nothing to be desired.

The method is essentially the collection of the oxygen of the perchlorate; its subsequent passage into an atmosphere of nitric oxide over a strong solution of hydriodic acid, and the titration of the iodine thus liberated with decinormal arsenic in alkaline solution. The apparatus employed consisted of a

piece of combustion tubing 10 or 12 cm. in length, drawn out at one end to a narrow constriction of length sufficient to prevent the action of the heat on the rubber tubing connecting it with a receiver filled with caustic potash. The tube must of course be cleansed from all organic materials and cannot be safely employed for more than three fusions. A platinum boat (porcelain fusing to the glass) served for the introduction of the perchlorate to the combustion tube, and in order to bring about a gradual and quiet fusion the perchlorate was covered with a small amount of an equal mixture of dry and pure sodium and potassium carbonates. Carbon dioxide obtained from a Kipp generator, the acid and marble of which had been previously boiled to expel all traces of air, and to which a little cuprous chloride had been added to take up any oxygen which might be absorbed from the top, was passed through a solution of iodine in potassium iodide to remove a trace of reducing agent which it was found to contain, and then washed with potassium iodide solution before being used. The larger end of the combustion tube was closed with a perforated rubber stopper by which it was attached to the carbon dioxide apparatus. After all air had been expelled from the inclined tube by means of carbon dioxide, it was connected by a short glass capillary and vacuum tubing joints with the receiver, into which about 50 to 100 cm^3 of gas was allowed to flow before the combustion was started and thus when only a small but inevitable bubble remained insoluble in the caustic potash the complete removal of air was indicated. To prevent the caustic potash from drawing into the combustion tube, a little more carbon dioxide was entered, when the current was closed by a pinch-cock on the side towards the generator and heat gradually applied — with perforated asbestos cards on either side to check its radiation to the rubber — and continued till the contents of the platinum boat was in a quiet state of fusion. By lowering one of the bulbs of the caustic potash receiver, the oxygen was evolved under slightly diminished pressure and thus the chances of loss decreased. Then the tube was again inclined and carefully annealed, while a current

of carbon dioxide carried all of the oxygen into the receiver, which was then closed and disconnected. As a receiver, two levelling bottles were found vastly superior to a burette; the glass stop-cocks of the latter giving continual trouble by the action of the caustic potash upon them. I found that gas could be removed from a levelling bottle without the loss of a particle if a perforated rubber stopper containing a capillary tube, which reached just even with the narrower end, was by a slight twist forced tightly into the neck of the bottle. In this way a regular funnel shape was obtained and the oxygen could be withdrawn without the slightest bubble remaining. The other end of the capillary was fitted with a short piece of vacuum tubing and screw pinch-cock, which worked incomparably better than the glass stop-cocks. The larger capacity of the bottle was favorable for the volume of oxygen evolved and its shape offered superior facilities for the absorption of carbon dioxide.

For the action of the oxygen on hydriodic acid through the medium of nitric oxide, various devices were tested. Passing it directly into nitric oxide over a solution of hydriodic acid in a Hempel absorption bulb was found to yield low and irregular results, due doubtless to the formation of nitric acid wherever the nitrogen tri-oxide, or per-oxide as the case might be, met water in which the hydriodic acid had been exhausted; as, for instance, along the sides of the bulb. Shaking the bulb as the oxygen entered improved the action, but was not sufficient. It was evident that for a complete action, the hydriodic acid solution must be strong and on the spot where the higher oxide of nitrogen is formed; and to avoid excessive use of the iodide the volume of water must be kept at a minimum. Letting a solution of hydriodic acid saturated with nitric oxide flow slowly into the Hempel bulb in which the oxygen was contained over water, was so slow in its action that a quantitative test was not applied. The plan of mixing the two gases under a strong solution of hydriodic acid by means of two capillaries with adjoining openings, was more effective and rapid, but it was wasteful of nitric oxide, which for

complete action would have to flow in continual excess, whereas only a small amount of nitric oxide would really be necessary for the reaction, since it could be used and reused for the transfer of free oxygen to the hydriodic acid. A simple piece of apparatus was then devised to meet all these conditions. It consisted of a 100 cm^3 bulb pipette, cut off short at either end with stop-cocks sealed to both stubs. The delivery tube of one of the stop-cocks was cut off rather short after being tapered and restricted so as to hold a rubber connector tightly, while the other delivery tube was left long enough to reach to the bottom of an Erlenmeyer beaker. It is a convenience to have these conducting tubes 3 or 4 mm. in diameter rather than capillaries, since for the various connections all air may be expelled from them by displacement with water, which is easily accomplished by using a long nozzled wash bottle. By attaching the shorter end to an ordinary water pump the air was partially exhausted when the stop-cock was closed and the bulb disconnected and lowered into a solution of hydriodic acid of approximately known strength, obtained by acidifying potassium iodide with hydrochloric acid. When the desired amount of liquid had been drawn in, the stop-cock was closed and connection made with the carbon dioxide, by which all residual air was expelled. Then the bulb, held so as to prevent the escape of the liquid, was again exhausted by attachment to the pump. After about 10 cm^3 of nitric oxide had been admitted, attachment was made to the receiver containing the oxygen, which was allowed to enter slowly under the diminished pressure within the bulb, and with continuous shaking of the contents of the latter. The latter precaution is essential to the process, as otherwise there is imperfect distribution of the hydriodic acid and the danger of forming nitric acid. But when the solution of hydriodic acid is kept strong and the shaking continued while the oxygen enters and for a minute or two afterward, depending on the rapidity with which it was admitted, the oxygen may be allowed to enter quite rapidly without any fear of imperfect action. The oxygen being immediately utilized, the partial vacuum is

affected only by the heat generated, which is scarcely noticeable. As a rule the bulb and contents were well cooled before the oxygen was admitted.

It is necessary of course to prevent the access of air into the bulb until the acid has been neutralized, to accomplish which, without loss of iodine, potassium carbonate must be used, at least for the end reaction. To remove the contents of the bulb for titration, the two delivery tubes were filled with water, after removing all sodium hydrate from the one through which the oxygen was entered; the shorter end connected to a supported funnel containing a saturated solution of bi-carbonate and the longer one inserted into an Erlenmeyer beaker containing a saturated solution of bicarbonate in amount sufficient — as previously determined — to neutralize all the acid taken. By opening that stop-cock the delivery tube of which reaches below the liquid in the beaker, the bi-carbonate is drawn in by the partial vacuum, with liberation of sufficient carbon dioxide to force all the liquid out. Owing to the consequent effervescence as the liquid gains its exit, the flow must be regulated by the stop-cock so as to avoid loss of iodine, which is prevented by inclining the beaker so that the bubbles strike against its side instead of being allowed to splatter out of the opening. To wash out the bulb, it is raised almost horizontally, so as to prevent the liquid from running through, and the upper stop-cock opened to admit the bicarbonate from the funnel. Both stop-cocks are then closed, the bulb disconnected and agitated, after which it may be washed with water and admission of air without any fear of liberating more iodine. An excess of decinormal arsenic is then run into the beaker and titrated back with iodine.

The many little precautions essential to note for the manipulation are in practice accomplished in a few moments. Seven determinations (not counting one which was all but completed, when an accident terminated it) from the weighing of the perchlorate to the titration, were completed in one day; and the results recorded in Table VII show with what reliability. In making the series of experiments recorded in

Table VII, it was found expeditious to have a partial vacuum always accessible instead of waiting each time for the exhaustion. This was obtained by connecting a vacuum flask with a two-holed stopper to an ordinary water pump, and having the other perforation fitted with a glass stop-cock. The bulb was merely attached to the vacuum by a piece of rubber tubing; the stop-cock opened and closed immediately, by which means a sufficient exhaustion was secured. To have the vacuum always in readiness a valve, described in a former

TABLE VII.

Exp.	$KClO_4$ taken.	KI taken.	HCl taken.	$KClO_4$ found.	Error.
	grm.	grm.	cm^3	grm.	grm.
(32)	0.1000	3	3	0.1003	0.0003+
(33)	0.1000	3	3	0.1006	0.0006+
(34)	0.1000	3	3	0.0998	0.0002−
(35)	0.1000	4	4	0.1003	0.0003+
(36)	0.1000	3	3	0.1003	0.0003+
(37)	0.1000	3	4	0.0999	0.0001−
(38)	0.1000	3	3	0.1003	0.0003+
(39)	0.1000	3	4	0.1001	0.0001+
(40)	0.1500	3	4	0.1493	0.0007−
(41)	0.2000	6	6	0.1999	0.0001−
(42)	0.2000	6	6	0.2009	0.0009+
(43)	0.0100	3	3	0.0099	0.0001−
(44)	0.0100	3	3	0.0100	0.0000
(45)	0.0000	3	3	0.0003	0.0003+

article of mine,* was placed in the rubber leading to the pump, and when lubricated with glycerine would hold the vacuum perfectly. The nitric oxide employed was supplied by a Kipp generator, in which globules of copper were acted upon by nitric acid mixed with an equal volume of water. To purify the gas evolved from any possible trace of the higher oxides, it was first passed through an acidified solution of potassium iodide in Geissler absorption bulbs, the last one of the three being alkaline. This method of generating nitric oxide in a Kipp generator (preferably charged with dilute acid and kept warm by immersion in hot water when

* Am. Jour. Sci., I, 132. This volume, p. 307.

large amounts of the gas are to be drawn at frequent intervals) was devised by Professor Gooch, by whom it has been employed for some time. It is automatic and eminently satisfactory. The hydriodic acid was obtained from a solution of potassium iodide containing one gram in ten cubic centimeters; thirty cubic centimeters being taken for each experiment, and acidified with the required amount of hydrochloric acid immediately before using, so as to prevent any liberation of iodine by the oxygen of the air. In those experiments in which more than this amount of potassium iodide was employed a correspondingly stronger solution of the latter was used, so that the volume of water was in all cases thirty cubic centimeters.

In experiments (40) and (43) during a momentary pause in the shaking of the bulb during the absorption, a black deposit of iodine began to form on the glass, and the result proves the importance of the precaution previously given, that the hydriodic acid should be kept hurling about the bulb until the action is completed. The blank determination (45) shows a constant error of the process which is about 0.0003 + and will be seen to correspond very closely to the average error of the determination. The cause is doubtless to be attributed to the trace of air which may remain in the bulb or be dissolved in the water. Since it can easily be determined and the correction made, it does not detract in any degree from the reliability of the determination.

To determine perchloric acid associated with other oxidizing agents it is only necessary to treat the mixture with the reagents which this investigation and the one referred to has shown to accomplish the reduction without affecting the perchlorate; subsequently evaporating to dryness and treating the residue according to the above process, viz., by heating in a current of carbon dioxide until decomposition is complete; collecting the oxygen over caustic potash; allowing it to enter a partial vacuum bulb containing a solution of potassium iodide, hydrochloric acid, and nitric oxide under constant agitation; and determining by means of a standard solution

of arsenic the amount of iodine set free. The method is proving applicable also to the determination of oxygen in air or wherever it may be obtained in the free state, unless diluted to such an extent with other gases that the vacuum would be filled by the diluent; even this contingency could be met by enlargement of the absorption bulb.

XLVI

THE REDUCTION OF SELENIC ACID BY HYDROCHLORIC ACID.

By F. A. GOOCH and P. S. EVANS, Jr.*

It has long been known that selenic acid is reducible by hydrochloric acid with evolution of chlorine, but the reaction was regarded as more or less uncertain until Petterson showed† that conditions of action may be secured under which the reduction proceeds so regularly that the chlorine evolved may be estimated iodometrically and taken as the measure of the selenic acid originally present, or of the selenious acid produced. According to this method of determination, it is only necessary to boil a solution of selenic acid in hydrochloric acid of moderate concentration, and if the solution is not too dilute the reduction is obtained in a few moments. Petterson did not, however, fix with exactness the limits of dilution within which a successful determination of the selenic acid may be expected. The object of this paper is to record the results which we have obtained in studying more closely the conditions necessary to an accurate and rapid reduction. We have used in our experiments solutions of selenic acid prepared by oxidizing pure, white, resublimed selenium dioxide according to the method laid down in a previous paper from this laboratory‡ for the quantitative determination of that substance. A portion of the crystalline oxide, approximately 2 grams, was carefully weighed, dissolved in 120 cm^3 of water containing one-twelfth of its volume of sulphuric acid, and treated with a strong solution of potassium permanganate until the color

* From Am. Jour. Sci., 1, 400.

† Zeitschr. anal. Chem., xii, 287.

‡ Gooch and Clemons: Am. Jour. Sci., 1, 51. This volume, p. 297.

characteristic of a distinct excess of that reagent prevailed distinctly over that of the brown oxide of manganese thrown down in the oxidation. The liquid was warmed to about 50° C., bleached by oxalic acid, and the excess of this reagent was destroyed by more permanganate. On account of the tendency of manganous salts, when present in considerable amount in warm solutions containing but little free acid, to react upon any considerable excess of permanganate with the deposition of higher oxides of manganese, it is generally necessary to repeat the bleaching and oxidizing process two or three times before the final color of a slight excess of the permanganate remains in clear solution and indicates the completion of the oxidation of the selenium. Finally, the liquid was filtered, diluted carefully to the volume of 1 litre, and used as a standard solution.

To determine in a general way the point of dilution at which mixtures of selenic and hydrochloric acids yield chlorine, we submitted various mixtures to distillation in a retort arranged with an inverted condenser (so that the aqueous distillate might be constantly returned to the retort) which was joined to an absorption apparatus charged with a solution of potassium iodide. A current of carbon dioxide was passed through the apparatus during the distillation, to carry forward whatever chlorine might be evolved in the process. The iodine liberated in the absorption apparatus was determined by

SeO_3 present.	Total volume.	Per cent of HCl, sp. gr. 1.20, by volume.	Time in minutes.	Chlorine in terms of the theoretical total.
grm.	cm^3			
0.1144	100	5	5	None.
0.1144	100	10	5	None.
0.1144	100	15	5	About 1%.
0.1144	100	20	5	About 7%.
0.1144	100	25	5	About 80%.
0.1144	100	30	5	About 70%.

titration with standard sodium thiosulphate. The results of these experiments are given in the accompanying table.

It is plain that so long as the volume of the hydrochloric

acid, sp. gr. 1.20, does not amount to more than ten per cent of the entire liquid no chlorine whatever is evolved and that only when the percentage of this acid rises as high as thirty does the chlorine evolved during boiling for five minutes approach the theoretical yield. In the ordinary process of distillation, in which the inverted condenser is not used, the liquid must gradually concentrate and the acid become stronger, so that under such conditions the yield of chlorine in a definite period of time must generally be greater than that obtained in the corresponding experiments of the table. Obviously it is advantageous, in attempting the practical reduction of selenic acid, to begin the distillation with acid of strength sufficient to insure the evolution of chlorine in quantity at the outset, and we have found it best to start with a mixture one-third of which is the strongest aqueous hydrochloric acid, sp. gr. 1.20. With solutions so constituted the reduction goes on rapidly. We have found, however, that care must be taken not to prolong the boiling after the solution reaches a concentration corresponding to hydrochloric acid of half-strength; for under such conditions — attained in our experiments either by boiling down mixtures of selenious acid and hydrochloric acid, or by making mixtures of selenious acid containing hydrochloric acid of half-strength — we have found that selenium appears visibly in the distillate, while iodine is set free from the iodide in the receiver. Good results may be expected when the mixture, containing one-third of its volume of the strongest aqueous hydrochloric acid at the beginning, is boiled until all chlorine is expelled, care being taken that the volume of the liquid shall not become less than two-thirds of the original volume.

These are conditions which are easily kept; and we have found that from solutions having a total volume of 75 cm^3 and containing 25 cm^3 of the strongest aqueous hydrochloric acid (sp. gr. 1.20), the entire amount of chlorine corresponding to the reduction of 0.2 grm. of selenic acid to selenious acid is liberated in ten minutes. The details of these experiments are given in the accompanying table.

Se = 79.1, O = 16.

SeO_2 taken.	Total volume at the outset.	HCl, sp. gr. 1.20, present.	Time in minutes.	SeO_2 found.	Error.
grm.	cm^3	cm^3		grm.	
0.0572	75	25	10	0.0568	0.0004—
0.0572	75	25	10	0.0569	0.0003—
0.1144	75	25	10	0.1143	0.0001—
0.1144	75	25	10	0.1137	0.0007—
0.1144	75	25	10	0.1147	0.0003+
0.2288	75	25	10	0.2288	0.0005—
0.2288	75	25	10	0.2279	0.0009—

XLVII

THE REDUCTION OF SELENIC ACID BY POTASSIUM BROMIDE IN ACID SOLUTION.

By F. A. GOOCH and W. S. SCOVILLE.*

It has been shown in previous papers from this laboratory that potassium bromide may be used with good effect in presence of acid and under well-defined conditions as a reducer of arsenic and telluric acids. This paper gives the results of similar experiments made to test the interaction between the bromide and selenic acid.

In our experiments we have used selenic acid carefully prepared by oxidizing pure, white, re-sublimed selenium dioxide by means of potassium permanganate in the manner described in the preceding paper. When intermixed with sulphuric acid and potassium bromide, selenic acid liberates bromine in proportion to the excess of acid, the bromide, and the elevation of the temperature. When such a solution is boiled the bromine is evolved and may be collected in potassium iodide contained in any appropriate receiver, and the iodine thus set free may be determined by standard sodium thiosulphate and taken as the measure of the bromine distilled. We have found an apparatus previously used in this laboratory in similar work (made by sealing the exit tube of a Voit wash-bottle, used as a retort, to the inlet tube of a Drexel wash-bottle used as a receiver, with a set of Will and Varrentrapp absorption bulbs sealed to the outlet tube of the receiver, to serve as a trap) extremely convenient in the distillation process, and a current of carbon dioxide passed slowly through the apparatus aids greatly in carrying the bromine to the receiver and in promoting quiet boiling. We

* From Am. Jour. Sci., 1, 402.

find that the applicability of the reaction to quantitative purposes turns upon the adjustment of the proportions of the reagents used. The following table contains the results obtained by varying the relative amounts of acid and bromide and the time of boiling. The selenium trioxide recorded as found is calculated upon the assumption that selenious acid, is the product of the reduction according to the equation,

$$H_2SeO_4 + 2HBr = H_2SeO_3 + H_2O + Br_2$$

$$Se = 79.1,\ O = 16.$$

Exp.	SeO_3 taken as H_2SeO_4.	H_2SO_4 of half-strength.	KBr taken.	Initial volume.	Final volume.	SeO_3 found.	Error.
	grm.	cm³	grm.	cm³	cm³	grm.	grm.
(1)	0.1145	5	1	60	25	0.1140	0.0005−
					15	0.1193	0.0048+
(2)	0.1145	5	5	60	30	0.1134	0.0011−
					28	0.1188	0.0043+
(3)	0.1145	10	1	60	27	0.1134	0.0011−
					23	0.1141	0.0004−
(4)	0.1145	20	1	60	35	0.1152	0.0007+
(5)	0.1145	20	1	60	35	0.1144	0.0001+
(6)	0.1145	20	5	60	45	0.1172	0.0027+

From these results it is apparent that the amount of iodine set free in the receiver is dependent upon the proportion of the bromide, the strength of the acid, and the degree of concentration during the distillation. When the proportions of sulphuric acid, potassium bromide, and selenic acid are favorable, the bromine liberated is removed rapidly to the distillate, leaving the residue perfectly colorless, but as the distillation is continued the liquid residue again takes on color and more iodine is set free by the action of the distillate upon a clear solution of potassium iodide, while selenium is plainly visible in the receiver. When the amount of potassium bromide is large its effect is to retain bromine in the liquid so obstinately that no period of colorlessness intervenes before the second stage of color arrives; when its amount is small while that of the sulphuric acid is also small, the reduction of the selenic acid

and the evolution of the bromine progress slowly; and when the amount of bromide is small while that of the acid is comparatively large, the interval of colorlessness is prolonged. The proportions which we found best in handling 0.25 grm. of selenic acid, or less, are an initial volume of 60 cm^3 containing 20 cm^3 of sulphuric acid of half-strength with 1 grm. of potassium bromide. Under these conditions we find, as in experiments (4) and (5) of the previous table, that the reduction is almost theoretically exact when the distillation is continued until the recoloration of the boiling liquid is distinctly recognizable; and this point corresponds in practice very closely to a concentration of volume to 35 cm^3. In the following table are gathered the results of further experiments in which these conditions of action were preserved:

SeO_3 taken as H_2SeO_4.	H_2SO_4 of half-strength.	KBr taken.	Initial volume.	Final volume.	SeO_3 calculated.	Error.
grm.	cm^3	grm.	cm^3	cm^3	grm.	grm.
0.0590	20	1	60	35	0.0588	0.0002–
0.0590	20	1	60	35	0.0591	0.0001+
0.0614	20	1	60	35	0.0616	0.0002+
0.0614	20	1	60	35	0.0607	0.0007–
0.1180	20	1	60	35	0.1177	0.0003–
0.1180	20	1	60	35	0.1180	0.0000
0.1534	20	1	60	35	0.1527	0.0007–
0.2349	20	1	60	35	0.2350	0.0001+

It is plain from these results that, if the conditions of action which we have indicated are observed, the reduction proceeds with regularity sufficient to warrant the use of the reaction as an analytical process.

XLVIII

THE IODOMETRIC DETERMINATION OF SELENIOUS AND SELENIC ACIDS.

By F. A. GOOCH and A. W. PEIRCE.*

It has been shown in a recent paper from this laboratory † that the simple contact of solutions of selenious acid, potassium iodide, and hydrochloric acid, according to the recommendation of Muthman and Schaefer, ‡ is not enough to effect the liberation of the theoretical amount of iodine when the assumption is made that the selenium of the selenious acid is all reduced to the elementary condition. On the other hand, it was found that the yield of iodine is complete when such mixtures are submitted to distillation under well-defined conditions. It is necessary, however, to estimate not only the iodine which passes to the distillate, but that which is retained in small proportion in the residue, and, though this method of proceeding yields closely accurate analytical results and is by no means difficult, it is obvious that a process so contrived that the reduction of the selenious acid should be registered entirely in the residue would possess the advantage in point of convenience. We have made the attempt, therefore, to apply in this case a principle of action laid down in a method elaborated in this laboratory for the estimation of chlorates.§ When a solution of arsenic acid containing potassium iodide and sulphuric acid is boiled under defined conditions ‖ the arsenic acid is reduced to arsenious acid with liberation of

* From Am. Jour. Sci., i, 31.

† Gooch and Reynolds, Am. Jour. Sci., l, 254. This volume, p. 310.

‡ Ber. Dtsch. chem. Ges., xxvi, 1008.

§ Gooch and Smith, Am. Jour. Sci., xlii, 220. This volume, p. 82.

‖ Gooch and Browning, Am. Jour. Sci., xl, 66. This volume, p. 30.

iodine. When the arsenic acid is in excess the whole of the iodine is evolved and the arsenious acid produced is its exact measure. Upon making the solution alkaline with acid potassium carbonate, the arsenious acid may be reoxidized by standard iodine, and the amount of iodine thus used will be the exact equivalent of that set free in the reduction-process. If, however, any other substance more easily reducible than arsenic acid is present, such substance should, naturally, take its part in liberating iodine from the iodide and the reduction of the arsenic acid should be correspondingly less. This was found to be the case when a mixture containing a chlorate, arsenic acid, potassium iodide, and sulphuric acid was boiled under regulated conditions, so that, with a knowledge of the amount of iodide employed and the determination of the quantity of iodine necessary to reoxidize the arsenious acid produced, the data were at hand for calculating the amount of chlorate present in the mixture. It was our hope (which proved to be well-founded, as the sequel shows) that selenious acid would behave like a chlorate under similar conditions.

Pure selenium dioxide was prepared by oxidizing presumably pure selenium in strong nitric acid, evaporating the solution to dryness, dissolving the residue in water, treating the solution with barium hydroxide until precipitation ceased, filtering, evaporating the filtrate to dryness, subliming the selenium dioxide from the residue, and resubliming that product in a current of dry oxygen (which we found to be vastly more convenient and effective than dry air) until it was perfectly white and crystalline. From the oxide thus made a standard aqueous solution was prepared, from which portions were measured and (for the sake of greater accuracy) weighed for use in the experiments to be detailed. To each weighed portion of the selenious acid, contained in an Erlenmeyer flask of 300 cm^3 capacity, was added a weighed amount of potassium iodide (somewhat in excess of that theoretically required) prepared in solution of convenient strength and tested as to its reducing power upon arsenic acid under the conditions of the experiment; a solution containing about

2 grm. of pure di-hydrogen potassium arseniate was introduced; and, finally, 20 cm^3 of sulphuric acid of half-strength. Protected from ordinary mechanical loss by a trap (consisting of a two-bulbed drying tube cut short and hung loosely with the wide end downward in the mouth of the flask) and from violent ebullition by the introduction of a few bits of porcelain, the liquid was boiled until the volume decreased according to indicating marks on the flask from 100 cm^3 or more to 35 cm^3 — concentration to about this lower limit having been found to be necessary to the completion of the reaction. The residue was cooled, the acid was nearly neutralized with potassium hydroxide, acid potassium carbonate was added until it was present to the amount of 20 cm^3 of its saturated solution in excess of the quantity needed to complete neutralization, and, after the addition of starch, standard iodine was introduced until the starch-blue appeared. The iodine introduced measured the arsenious acid (and so the quantity of iodine set free by the arsenic acid), and the difference between it and the iodine originally present in the form of the iodide represents the amount set free by the selenious acid.

The following table comprises the details and results of a series of determinations made in the manner outlined:

$$Se = 79.1,\ O = 16$$

Initial volume.	Final volume.	H_2SO_4 half-strength.	Di-hydrogen-potassium arseniate.	KI taken.	SeO_2 taken.	SeO_2 found.	Error.
cm^3	cm^3	cm^3.	grm.	grm.	grm.	grm.	grm.
100	35	20	2	1.3277	0.1280	0.1275	0.0005—
100	35	20	2	1.0429	0.0998	0.0994	0.0004—
100	35	20	2	1.0887	0.1024	0.1028	0.0004+
100	35	20	2	1.0405	0.1036	0.1028	0.0008—
100	35	20	2	1.0721	0.1030	0.1029	0.0001—
100	35	20	2	0.9958	0.1273	0.1272	0.0001—
125	35	20	2	2.0828	0.1997	0.2000	0.0003+
125	35	20	2	2.2272	0.2110	0.2113	0.0003+
125	35	20	2	2.1535	0.2067	0.2069	0.0002+
150	40	20	2	2.6554	0.2560	0.2549	0.0011—
175	35	20	2	3.2428	0.3110	0.3118	0.0008+
175	35	20	2	3.2428	0.3085	0.3083	0.0002—

Obviously the reduction of selenious acid by this method is regular and accurate.

When similar treatment was applied to selenic acid it became apparent that the arsenic acid attacked and destroyed the iodide before the selenic acid had been completely reduced. It is plain, therefore, that the selenic acid must be reduced to the condition of selenious acid before its estimation by the iodide method can be attempted. Ordinarily the simplest mode of reducing selenic acid is by boiling it in solution with hydrochloric acid of definite strength,* but in this case the presence of hydrochloric acid is precluded on account of the consequent volatilization of arsenious chloride during the process of concentration in the subsequent treatment with the iodide. It has been shown, however, in a recent paper from this laboratory † that selenic acid is easily and completely reduced to selenious acid by potassium bromide and sulphuric acid under defined conditions. Moreover, arsenious bromide is not volatilized appreciably under the conditions. We made the attempt, therefore, to effect the iodometric determination of selenic acid by first reducing it to selenious acid by the bromide process and then treating the residue with arsenic acid and potassium iodide in the manner described.

Selenic acid was prepared in standard solution by treating a known weight of pure resublimed selenium dioxide by a strong solution of potassium permanganate, in presence of a moderate amount of sulphuric acid, until the purple color was distinctly visible, dissolving the precipitated oxide of manganese by oxalic acid, again adding permanganate until the final color of faintly visible pink was permanent for a half-hour or more, and diluting to a fixed volume. Portions of the solution of selenic acid were measured into counterpoised Erlenmeyer flasks of 300 cm^3 capacity and weighed, 1 grm. of potassium bromide was added, and sulphuric acid in such quantity that the total amount of the free acid should correspond to 20 cm^3 of the acid of half-strength. The

* Gooch and Evans, Am. Jour. Sci., 1, 400. This volume, p. 331.

† Gooch and Scoville, Am. Jour. Sci., 1, 402. This volume, p. 335.

solution possessing a volume of 60 cm^3 to 100 cm^3 was boiled until the clear, colorless solution left when the bromide vanished began to color again. Experience showed that the reappearance of the brownish color is very easily seen and that it is not safe to conclude that all free bromine has been eliminated, under the conditions of dilution and proportion, until this stage of concentration — which corresponds to a volume of about 35 cm^3 — has been reached; but the distillation should not be pushed beyond the point at which the returning color is noted. When this condition was reached the solution was cooled, and treated exactly in the manner described for the reduction of selenious acid. The neutralization by acid potassium carbonate, after the final boiling, generally occasioned the precipitation of manganous carbonate, but the precipitate did not interfere in the slightest with the titration which followed.

The following table comprises the determinations which were made to test the accuracy of the iodometric determination of selenic acid by the combined processes of reduction.

SeO_3 taken as H_2SeO_4.	KI used in second reduction.	SeO_3 found.	Error.
grm.	grm.	grm.	grm.
0.0378	0.6306	0.0380	0.0002+
0.0378	0.5643	0.0374	0.0004—
0.0516	0.7186	0.0517	0.0001+
0.0503	0.7302	0.0508	0.0005+
0.0541	0.6671	0.0544	0.0003+
0.1007	1.8277	0.1011	0.0004+
0.1008	1.8277	0.1011	0.0003+
0.1007	1.2082	0.1005	0.0002—
0.1007	1.1684	0.1016	0.0009+
0.1007	1.0522	0.0999	0.0008—
0.1009	1.2679	0 1005	0.0004—
0.1031	1.1119	0.1032	0.0001+
0.1870	1.8720	0.1879	0.0009+
0.2014	1.9915	0.2020	0.0006+
0.2016	2.0745	0.2025	0.0009+
0.2059	1.8687	0.2064	0.0005+

It is plain, therefore, that selenic acid may be determined iodometrically with accuracy by first reducing it to the

condition of selenious acid by treatment with potassium bromide in presence of sulphuric acid, in the manner described, and then completing the reduction to the elementary condition by the treatment with potassium iodide and potassium arseniate.

XLIX

ON THE INTERACTION OF CHROMIC AND ARSENIOUS ACIDS.

By PHILIP E. BROWNING.*

KESSLER † has shown that arsenious acid may be determined by treating it, in the presence of hydrochloric acid, with an excess of a chromate solution of known strength, by which treatment the arsenious acid is oxidized and the chromic acid reduced. The excess of the chromic acid is then determined by the addition of a ferrous salt of known strength until a drop taken from the solution gives a blue color with a ferricyanide. Chromic acid is then added again until the blue color disappears. The amount of the chromate originally used less the excess determined by the ferrous salt gives the amount of the chromate used for the oxidation, from which may be calculated the amount of arsenious acid originally present. Despite the use of a ferrous salt and the numerous steps involved in the manipulation, Kessler claims very satisfactory results for his method. The object of this paper is to give the results of some experiments in which Kessler's reaction was used for the reverse process, the arsenious acid being used in excess, according to the reaction:

$$4CrO_3 + 3As_2O_3 + (X)As_2O_3 = 2Cr_2O_3 + 3As_2O_5 + (X)As_2O_3$$

For the work, a solution of potassium dichromate was made, the standard of which was determined by evaporating definite portions measured from a burette into previously weighed and counterpoised crucibles, heating just to the melting point, and weighing after cooling. A decinormal solution of arsenious acid was made in the usual manner, as was also a

* From Am. Jour. Sci., i, 35. † Ann. Phys. clxxi, 204 (1855).

decinormal iodine solution which was standardized frequently in course of the work against the arsenious acid. The method of manipulation was as follows: Definite portions of the chromate solution were measured from a burette into counterpoised flasks and weighed, as a check on the burette reading, about 10 cm^3 of dilute hydrochloric or sulphuric acid (1–4) added, and a carefully measured amount of the arsenious acid solution — care being taken to have an excess of the amount necessary for the reaction. After a few moments the reduction seemed complete, the solution having taken on the bluish green color characteristic of the chromium salts. The application of heat was found to be unnecessary, the reaction going on quickly and completely, as it seemed, in the cold. The solution was then treated with acid potassium or sodium carbonate (about 5 grm.) in excess. At this point a precipitate formed unless Rochelle salts had been added, as was sometimes the case, to prevent it. To the alkaline solution iodine was added until a yellow tinge showed it to be in excess, and the solution was allowed to stand, with frequent shaking, about one-half hour, at the end of which time the excess of the arsenious acid was thoroughly acted upon. In order to test the permanency of the iodine color in alkaline solution, two experiments were made, in the first of which 5 grm. of acid sodium carbonate were dissolved in about 100 cm^3 of water, and in the second the amount of acid generally used (10 cm^3) was neutralized with the acid carbonate and an excess added, the amount of water present being about the same as in the first experiment. Starch and a drop of iodine solution were then added. No bleaching effect was apparent during two hours. Several experiments, made without allowing the solution to stand, with the excess of iodine seemed to show that the excess of the arsenious acid had not been completely oxidized by the iodine. As this took place mainly in those experiments in which the precipitate had not been held up by Rochelle salts, I am inclined to attribute it to the holding of the arsenious acid by the precipitate. After this point in the process had

been reached, the excess of iodine was destroyed by the addition of arsenious acid, starch was added and the blue color obtained with iodine. Knowing the amount of arsenious acid originally added together with the second amount, used to bleach the excess of iodine, also the total amount of iodine employed and its value in terms of arsenious acid, we are in position to determine the amount of arsenious acid used for the reduction; and, by referring to the reaction given above we can calculate the amount of chromic acid originally present. The use of Rochelle salts had a disadvantage, however, which should be mentioned. If the precipitate is held up, the solution takes on a dark green color which makes the starch iodide reaction difficult to detect. The presence of the precipitate, except for the apparent holding of some arsenious acid — a source of error which seems to be largely obviated by the standing with the excess of iodine — causes no inconvenience, being itself of a very light green color and leaving the solution almost colorless. I have tried filtering with no gain in convenience, since the precipitate is of a gelatinous character and filters very slowly, so that the filtration and thorough washing lengthen the process very materially.

The results follow in the table:

Exp.	CrO_3 taken.	CrO_3 found.	Error.	Remarks.
	grm.	grm.	grm.	
(1)	0.1001	0.1004	0.0003+	
(2)	0.1005	0.1004	0.0001−	The iodine acted 20 minutes.
(3)	0.1006	0.1007	0.0001+	" " "
(4)	0.1004	0.1011	0.0007+	" " "
(5)	0.1009	0.1009	0.0000	" " 2 hours.
(6)	0.1002	0.1003	0.0001+	" " "
(7)	0.1011	0.1004	0.0007−	Rochelle salts used.
(8)	0.1007	0.1007	0.0000	" "
(9)	0.0401	0.0395	0.0006−	
(10)	0.0402	0.0388	0.0014−	0.5 grm. ferric alum present.
(11)	0.1001	0.1018	0.0017+	
(12)	0.1009	0.1007	0.0002−	
(13)	0.1007	0.1011	0.0004+	1 grm. ferric alum present.
(14)	0.1005	0.1017	0.0012+	
(15)	0.1004	0.1010	0.0006+	
(16)	0.1000	0.1032	0.0032+	Rochelle salts used.
(17)	0.1005	0.1006	0.0001+	1 grm. ferric alum present.

In three of the above experiments the process was carried through in the presence of a ferric salt with fairly successful results. The presence of the brown precipitate, however, makes the end reaction rather difficult to determine. If, however, the precipitate be allowed to settle after each addition of iodine, the color can be detected very readily in the supernatant liquid.

Among volumetric processes of great delicacy this process naturally does not find its place. It is, however, interesting to know to what degree the reaction may be depended upon for analytical purposes.

L

A METHOD FOR THE SEPARATION OF SELENIUM FROM TELLURIUM, BASED UPON THE DIFFERENCE IN VOLATILITY OF THE BROMIDES.

By F. A. GOOCH and A. W. PEIRCE.*

It has been shown in previous articles from this laboratory † upon the reducibility of selenic acid by the action of the halogen acids, that when small amounts of selenic acid are boiled in aqueous solution with potassium iodide and hydrochloric acid, selenium is precipitated, while the iodine set free simultaneously may be collected in the distillate, estimated, and taken as the measure of the selenic acid originally present; that if the iodide is omitted from the mixture, so that the hydrochloric acid alone shall be the reducer, the reduction proceeds only to the point of formation of selenious acid, provided the boiling is not continued after the hydrochloric acid has reached the condition of half-strength at which it boils unchanged under normal atmospheric pressure; and that a solution of selenic acid, potassium bromide, and sulphuric acid of regulated dilution and proportions also yields under defined conditions selenious acid as the product of reduction. When, however, the ebullition of a solution of selenious acid in hydrochloric acid is continued after the acid has reached the condition of half-strength, traces of selenium appear in the receiver and connecting tubes, the distillate sets free iodine from potassium iodide, and it is evident that the selenious acid is undergoing further reduction. So also when the boiling of the mixture of sulphuric acid, potassium bromide, and selenious acid is pressed beyond

* From Am. Jour. Sci., i, 181.

† Am. Jour. Sci., l, 254, 400, 402. This volume, pp. 310, 331, 335.

the point at which the solution begins to be colored, selenium appears in traces in the tube leading to the receiver and the distillate liberates iodine from an iodide. Obviously the conditions have been at this time reached in the processes of concentration when selenium tetrachloride and selenium tetrabromide, respectively, are forming from the acid, and the appearance of the elementary selenium is due to partial decomposition of the halogen salts. We have observed more recently phenomena of a similar nature (as would naturally be expected under the conditions), when aqueous solutions of selenious acid, phosphoric acid, and sodium chloride are submitted to distillation: that is to say, there comes a time in the process of boiling such mixtures when the appearance of elementary selenium and the action of the distillate upon potassium iodide make evident the volatilization and partial decomposition of the selenium compounds of the halogens, and the further continuance of the treatment results in the more or less complete removal of the selenium compounds to the distillate. From the mixture containing the phosphoric acid, selenious acid, and sodium chloride we have been able to secure only a partial volatilization of the selenium chloride. The transfer of the selenium bromide, however, from the mixture of the acids and potassium bromide is rapid and complete, and this fact points out a possible method for the separation of selenium from substances which do not form volatile products under similar conditions of treatment. Tellurium proves to be such a substance, and the work to be detailed has to do with a process for the separation of selenium from tellurium, based upon the volatility of selenium tetrabromide and the non-volatility of tellurium tetrabromide under definite conditions.

The selenious acid which we used was made by dissolving in water a known weight of the white, crystalline, anhydrous dioxide prepared from pure selenium by oxidation with nitric acid, treatment in solution with barium hydroxide to remove selenic acid, and repeated sublimation in a current of oxygen. The tellurium was obtained in solution in its lower condition

of oxidation by dissolving in potassium hydroxide a known weight of tellurium dioxide (made by oxidizing presumably pure tellurium by nitric acid and igniting the product at a low red heat), neutralizing with phosphoric acid, and redissolving in a sufficient excess of that acid the precipitate formed in the process of neutralization.

In our preliminary experiments we made use of a form of apparatus previously employed for similar purposes and described in former articles from the laboratory, viz.: a Voit flask, serving as the retort, sealed to the inlet tube of a Drexel wash-bottle, used as a receiver, the outlet tube of which was trapped by sealing on Will and Varrentrapp absorption bulbs. Later the apparatus was changed to the form shown in the accompanying figure by introducing a second Voit flask, in order that the selenium might be estimated in the distillate more conveniently.

FIG. 14.

Into the first Voit flask, V^1, were put measured amounts of the solution of selenious acid with 20 cm^3 of syrupy phosphoric acid (sp. gr. 1.70), 1 grm. of potassium bromide, and water enough to make the entire volume of liquid 50 cm^3. The second flask, V^2, contained about 15 cm^3 of water, and was kept cool by immersion in water. The Drexel bottle and bulbs contained a solution of potassium iodide. A current of carbon dioxide was passed slowly through the apparatus to secure quiet ebullition and to aid in the transfer of the distillate to the receiver. Upon applying heat to the first flask, V^1, the solution boiled quietly and without change until the volume of liquid had decreased to about 30 cm^3, when traces of red selenium began to deposit in the tube joining the first and second flasks. When the volume had further diminished to about 25 cm^3 the liquid began to take on color, darkened rapidly, and evolved bromine, which at once attacked

the selenium previously deposited. The greater part of the bromine was absorbed in the second flask, V^2, but a trace found its way to the Drexel bottle, in which it set free a slight amount of iodine from the iodide, as was afterward proved by the effect upon starch. As the operation progressed an orange-yellow crystalline solid, presumably selenium tetrabromide for the most part, appeared in the tube where the selenium had been, while a dark oily liquid, consisting largely, no doubt, of the monobromide, condensed in drops upon the walls of the flask and returned to form a floating layer upon the hot liquid. Finally, when the volume had diminished to 15 cm^3, the liquid had become perfectly clear and colorless, white fumes of hydrobromic acid were evolved, and the tube between the two flasks had been cleared. At this point the operation was stopped and the apparatus allowed to cool. The addition of potassium iodide to the contents of the first flask neither liberated iodine nor precipitated selenium, and so proved that no reducible compound of selenium still remained in that flask. The amount of selenium which had been volatilized we determined directly by means of a method worked out in this laboratory and to which reference has already been made.* We introduced into the second flask, V^2, which now contained (beside a trace of selenium corresponding to the slight amount of bromine which had escaped to the Drexel bottle) the colorless selenious acid regenerated by the action of the water and free bromine upon the mixed bromides which had distilled, 1 grm. of potassium iodide and 5 cm^3 of hydrochloric acid and, after removing the first flask, V^1, and connecting the carbon dioxide generator with the inlet tube of V^2, boiled the solution ten minutes while a current of carbon dioxide passed through this apparatus. At the end of this time the iodine set free by the action of the iodide had been almost completely removed to the Drexel bottle, leaving a nearly colorless solution containing particles of dense, crystalline selenium.

* Gooch and Reynolds, Am. Jour. Sci., 1, 254. This volume, p. 310.

The iodine in the receiver, including of course the small amount set free by the bromine which reached the receiver in the first stage of the process, together with the small amount remaining in the flask, was titrated with sodium thiosulphate and taken as the measure of the selenium dioxide acted upon originally. In this way we obtained the following results:

SeO_2 taken.	SeO_2 corresponding to iodine found.	Error.
grm.	grm.	grm.
0.0366	0.0372	0.0006+
0.0366	0.0377	0.0011+
0.1098	0.1090	0.0008−
0.1098	0.1101	0.0003+

It is obvious from these results that the iodine finally found in the receiver is actually an accurate measure within reasonable limits of the selenium dioxide originally put into V^1 and volatilized therefrom by the action of phosphoric acid and potassium bromide.

When tellurium dioxide is subjected to similar treatment the phenomena are different. The solution containing the tellurous acid, potassium bromide, and phosphoric acid, in the proportions used in the experiments with selenious acid, colors at about the same degree of concentration at which the solution containing the selenious acid began to darken. As the concentration progresses the color deepens, ruby red crystals (probably hydrated tellurium tetrabromide) form, which accumulate upon the walls of the flask and turn yellow, and when the volume of the solution is diminished to 15 cm^3 a green vapor begins to distil. During the process no iodine is set free in the Drexel bottle, and upon stopping the boiling we found that the addition of potassium iodide to V^2 liberated no iodine, even when the boiling had gone so far that a trace of the green vapor had condensed and run into the water in the flask. In view of these facts it seemed probable that the process of treatment which we have

described might be applied to the determination of selenium associated with tellurium. In the following experiments, made to test the point, tellurium dioxide was weighed out and dissolved in strong potassium hydroxide, the alkali was neutralized and the precipitate thus formed was redissolved by phosphoric acid, and 20 cm^3 of the acid of sp. gr. 1.70 were added in excess. To the solution were added definite amounts of selenium dioxide taken in a standardized solution and 1 grm. of potassium bromide, and the whole was introduced into the first flask, V^1, with enough water to make the entire volume of the solution 50 cm^3. The second flask, V^2, contained 10 cm^3 of water, and the Drexel bottle and trap were charged with a solution of potassium iodide. Carbon dioxide was passed through, and the solution in V^1 was boiled. The phenomena of each individual set of experiments with the selenious and tellurous acids occurred now together — the coloring of the liquid, the evolution of bromine, the distillation of the selenium bromides, the crystallization of the tellurium tetrabromide, the disappearance of the selenium compounds from the connecting tube. The distillation was stopped when the volume of the residue had diminished to 15 cm^3. After cooling, the first flask V^1 was removed, 1 grm. of potassium iodide and 5 cm^3 of hydrochloric acid were added to the contents of the second flask, V^2, the current of carbon dioxide was again started through the apparatus, the mixture was boiled ten minutes, and the iodine in the flask, receiver, and trap was determined by titration with sodium thiosulphate and taken as the measure of the selenium dioxide. In some preliminary experiments trouble was experienced in removing the last traces of the selenium bromides held back mechanically by the oily tellurium compound which collected upon the walls of the distillation flask and in the connecting tube; but the difficulty was satisfactorily overcome by cloaking the flask with a mantle of asbestos board and flaming the connecting tube gently toward the close of the process of distillation. The results obtained are gathered in the following table:

TeO_2 taken.	KBr taken.	H_3PO_4 (Sp. gr. 1.70) taken.	Final volume.	SeO_2 taken.	SeO_2 found.	Error.
grm.	grm.	cm^3	cm^3	grm.	grm.	grm.
0.1	1	20	15	0.0733	0.0735	0.0002+
0.1	1	20	15	0.0997	0.0995	0.0002—
0.1	1	20	15	0.1004	0.1003	0.0001—
0.1	1	20	15	0.0916	0.0914	0.0002—
0.1	1	20	15	0.0997	0.0995	0.0002—
0.1	1	20	15	0.1010	0.1014	0.0004+
0.1	1	20	15	0.1015	0.1008	0.0007—
0.1	1	20	15	0.1019	0.1022	0.0003+
0.1	1	20	15	0.1010	0.1012	0.0002+
0.1	1	20	15	0.1002	0.1000	0.0002—
0.1	1	20	15	0.1006	0.1004	0.0002—
0.1	1	20	15	0.1006	0.1001	0.0005—

Obviously the error of the process, when carefully conducted and applied to the amounts of material which we have employed, is very small.

LI

THE ACTION OF UREA AND SULPHOCARBANILIDE ON CERTAIN ACID ANHYDRIDES.

By FREDERICK L. DUNLAP.*

In 1882, Piutti,† in an article on "urea and thiourea derivatives of phthalic acid," showed that phthaluric acid was the product of the reaction of urea on phthalic anhydride when equal molecules were heated to 110–120° C. At a higher temperature he found that the phthaluric acid decomposed into phthalimide with the liberation of carbon dioxide and ammonia. The two stages in the formation of the imide are shown in the following equations:

$$C_6H_4\begin{cases}CO\\CO\end{cases}>O + NH_2CONH_2 = C_6H_4\begin{cases}CONHCONH_2\\COOH\end{cases}.$$

$$C_6H_4\begin{cases}CONHCONH_2\\COOH\end{cases} = C_6H_4\begin{cases}CO\\CO\end{cases}>NH + CO_2 + NH_3.$$

I have found that the reaction passes directly through both stages to the formation of phthalimide if the temperature of the mixture of phthalic anhydride and urea be raised at once to 150°, the imide thus obtained being nearly pure.

Phthalimide.—Ten grams of urea (1 molecule) and 25 grams of phthalic anhydride (1 molecule) were heated in a half liter flask, in an oil-bath, until the bath showed a temperature of 150°. At this temperature the contents of the flask became entirely liquid, and ammonia and carbon dioxide were evolved. After heating at this temperature for

* From Am. Chem. Jour. xviii, 332.
† Ann. Chem. (Liebig), ccxiv, 20.

several minutes, the contents of the flask suddenly solidified. The solid contents of the flask were then treated with boiling water, to free the phthalimide from any unchanged urea or phthalic anhydride. The phthalimide thus prepared was perfectly white and melted without further purification at 227°. When pure, phthalimide melts at 229° (uncorrected) and upon analysis gave the following results:

0.2058 gram substance gave 0.4915 gram CO_2 and 0.0656 gram H_2O.

	Calculated for $C_8H_5O_2N$.	Found.
C	65.31	65.12
H	3.40	3.54

Obviously, this method is a good one for making phthalimide, as the product obtained is practically pure, and only a few minutes are necessary for its preparation. A 90 per cent yield was obtained.

In hopes that a new and general method for the preparation of imides could be obtained by the action of urea upon anhydrides, this action of urea was studied further upon dichlormaleïc anhydride, dibrommaleïc anhydride and succinic anhydride.

Dichlormaleïnuric Acid. — When a mixture of equal molecules of urea and dichlormaleïc anhydride was heated in a bath to 70°, the mixture began to melt. When the temperature of the bath was raised to 90–95° and held constant for about five minutes the liquid mixture of anhydride and urea solidified. This temperature of 90–95° was maintained for twenty minutes. The solid product thus obtained was washed with a small quantity of cold water and then recrystallized from alcohol. It recrystallized from alcohol in transparent prisms having truncated ends, and had a melting-point of 158°. When this pure product — dichlormaleïnuric acid — melts, it gives off gas and again solidifies in the melting-point tube, remelting at 179°, the melting-point of dichlormaleïnimide. It is very sparingly soluble in all the ordinary solvents except

water, in which it dissolves when heated. Nearly a 50 per cent yield was obtained.

0.1917 gram substance gave 0.2415 gram AgCl.

	Calculated for $C_2H_4O_4N_2Cl_2$.	Found.
Cl	31.28	31.15

Dichlormaleïnimide. — Five grams of dichlormaleïc anhydride and 3 grams of urea (equal molecules) were heated in a flask, the temperature of the oil-bath being raised to 110–115°. The contents of the flask were liquid at this temperature, and ammonia and carbon dioxide were freely evolved. After heating for fifteen minutes at this temperature the contents of the flask were allowed to cool, and the solid product washed with a small quantity of cold water. One gram of dichlormaleïnimide remained after this washing. When pure, the dichlormaleïnimide melted at 179°, and upon analysis gave the following results:

0.2136 gram substance gave 0.3700 gram AgCl.

	Calculated for $C_4Cl_2O_2NH$.	Found.
Cl	42.78	42.83

We have here, in the formation of dichlormaleïnimide from dichlormaleïc anhydride and urea, a reaction exactly similar to the one in which phthalimide is formed. The first stage of the reaction consists first in the addition of urea to dichlormaleïc anhydride to produce dichlormaleïnuric acid.

$$\begin{matrix} ClC-CO \\ \| \\ ClC-CO \end{matrix} >O + NH_2CONH_2 = \begin{matrix} ClC-CONHCONH_2 \\ \| \\ ClC-COOH. \end{matrix}$$

This dichlormaleïnuric acid, upon being heated to its melting-point, loses ammonia and carbon dioxide with the formation of dichlormaleïnimide,

$$\begin{matrix} ClC-CONHCONH_2 \\ \| \\ ClC-COOH \end{matrix} = \begin{matrix} ClC-CO \\ \| \\ ClC-CO \end{matrix} >NH + NH_3 + CO_2.$$

Dibrommaleïnuric Acid. — A mixture of equal molecules of urea and dibrommaleïc anhydride were heated in an oil-bath, When the bath registered 90° the contents of the flask began to melt. The temperature was raised to 100–105°, at which point it was kept until the liquid contents of the flask had become solid again. After cooling, this solid product was washed with water and purified by recrystallization from alcohol. When pure it is perfectly white and melts at 191° with gas evolution. After melting, the liquid contents of the tube resolidified and again melted at 221°, which is 4° low for the melting-point of dibrommaleïnimide. This low melting-point is explained by the fact that the dibrommaleïnuric acid, upon melting, does not entirely break down into ammonia, carbon dioxide, and dibrommaleïnimide, as is seen by the darkening of the contents of the melting-point tube. The presence of impurities would naturally tend to lower the melting-point of the dibrommaleïnimide. Nearly a 50 per cent yield of dibrommaleïnuric acid was obtained. It crystallized in bunches of small prisms having doubly truncated ends.

0.2117 gram substance gave 0.2512 gram AgBr.

	Calculated for $C_5H_4Br_2N_2O_4$.	Found.
Br	50.63	50.51

I found this acid to be readily soluble in acetone; tolerably soluble in chloroform and ether; insoluble in ligroïn, benzol, carbon bisulphide and water.

Dibrommaleïnuric acid corresponds exactly to dichlormaleïnuric acid, being formed by the addition of urea and dibrommaleïc anhydride.

$$\begin{matrix} BrC-CO \\ \| \quad >O \\ BrC-CO \end{matrix} + NH_2CONH_2 = \begin{matrix} BrC-CONHCONH_2 \\ \| \\ BrC-COOH \end{matrix}.$$

Dibrommaleïnimide. — When equal molecules of dibrommaleïc anhydride and urea were heated up gradually to 135°, the mass turned very dark in color, and ammonia and carbon dioxide were evolved. After the evolution of gas had ceased, the then

solid contents of the flask were extracted with hot alcohol, filtered from the insoluble portion, treated with bone-black, and then evaporated to small bulk, and the dibrommaleïnimide allowed to crystallize out. It was further purified by crystallization from alcohol. No analysis of this dibrommaleïnimide was made, because its crystalline form, melting-point and method of formation were definite enough for identification. A twenty-four per cent yield was obtained.

The formation of dibrommaleïnimide from dibrommaleïc anhydride and urea is exactly similar to the formation of dichlormaleïnimide when urea and dichlormaleïc anhydride are used, therefore no new equations are necessary to represent this imide formation.

Succinimide. — Ten grams of succinic anhydride and 6 grams of urea were heated in a distilling-flask. As the temperature rose the contents of the flask melted and, finally, began to darken, ammonia and carbon dioxide being freely evolved. As the temperature was raised a slightly yellowish distillate, boiling above 280°, was obtained. This distillate immediately solidified and was further purified by recrystallization from anhydrous acetone. It had a melting-point of 124° and was perfectly white. A 40 per cent yield of succinimide was obtained. Upon analysis it gave the following result:

0.2099 gram substance gave 0.3751 gram CO_2 and 0.1019 gram H_2O.

	Calculated for $C_4H_5O_2N$.	Found.
C	48.49	48.73
H	5.05	5.39

Pike, who first made succinuric acid* states that it melts with complete decomposition. In hopes of finding succinimide as one of these products of decomposition, succinic acid was prepared according to Pike's method, and upon purification was found to have a melting-point of 211–211.5°, and not 203–205°, as Pike gives it. When pure succinuric acid was subjected to distillation it acted as did the mixture of succinic

* Ber. Dtsch. chem. Ges., vi, 1104.

anhydride and urea. The succinuric acid melted with the evolution of ammonia and carbon dioxide, and turned quite dark. A distillate, boiling above 280°, was obtained, which was easily identified as succinimide.

Having obtained succinimide from succinuric acid, this shows us how the succinimide is formed by the action of urea upon succinic anhydride. When this mixture is heated succinuric acid is first formed. This breaks down at a higher temperature with succinimide, carbon dioxide, and ammonia as its products. The formation of succinimide is represented by the following equations:

$$\begin{matrix} CH_2-CO \\ | \\ CH_2-CO \end{matrix} >O + NH_2CONH_2 = \begin{matrix} CH_2-CONHCONH_2 \\ | \\ CH_2-COOH \end{matrix}.$$

$$\begin{matrix} CH_2-CONHCONH_2 \\ | \\ CH_2-COOH \end{matrix} = \begin{matrix} CH_2-CO \\ | \\ CH_2-CO \end{matrix} >NH + NH_3 + CO_2.$$

Action of Sulphocarbanilide on Phthalic Anhydride.

The action of a substituted urea, sulphocarbanilide, on phthalic anhydride was next studied. It was hoped that a diphenylthiophthaluric acid might be obtained in this way, and the evidence goes to show that it was formed, but that decomposition ensued immediately at the temperature of the reaction. I found as product of the reaction at 125–130°, phthalanilic acid and phenyl mustard oil. The formation of the phthalanilic acid can best be explained by the following equations:

$$C_6H_4\begin{matrix} CO \\ \diagup\diagdown \\ CO \end{matrix}>O + NHC_6H_5CSNHC_6H_5 = C_6H_4\begin{matrix} CONC_6H_5CSNHC_6H_5 \\ \diagup\diagdown \\ COOH \end{matrix}.$$

$$C_6H_4\begin{matrix} CONC_6H_5CSNHC_6H_5 \\ \diagup\diagdown \\ COOH \end{matrix} = C_6H_4\begin{matrix} CONHC_6H_5 \\ \diagup\diagdown \\ COOH \end{matrix} + SCNC_6H_5.$$

At 170–175° phthalanil, carbonic oxysulphide, and aniline are the products.

Phthalanilic Acid. — Five grams of phthalic anhydride and 7.7 grams of sulphocarbanilide, equal molecules, were heated in an oil-bath until the bath showed a temperature of 125–130°. The contents of the flask liquefied, and, after a few minutes' heating, began to solidify. The heating was carried on at 125–130° for twenty minutes more. During this heating a very small amount of carbonic oxysulphide was evolved.

The solid product was then washed with a small amount of cold alcohol and the product thus obtained purified by recrystallization from alcohol. The pure product melted at 169–169.5°, and then gave off gas, resolidifying in the melting-point tube, and remelting at 204°, the melting-point of phthalanil. The first alcoholic washings contained quantities of phenyl mustard oil, which was identified by its boiling-point and other properties. After the first treatment with alcohol the product was perfectly white and nearly pure. A 60 per cent yield was obtained. The phthalanilic acid so prepared crystallized from alcohol in small prisms, and upon analysis gave the following results:

0.2090 gram substance gave 0.5366 gram CO_2 and 0.0865 gram H_2O.

	Calculated for $C_{14}H_{11}O_3N$.	Found.
C	69.71	70.03
H	4.56	4.60

Phthalanilic acid is insoluble in benzol and chloroform; very sparingly soluble in acetone; insoluble in ligroïn and ether; practically insoluble in cold water, but slightly soluble in boiling water, from which it separates upon cooling.

Phthalanil. — Five grams of phthalic anhydride and 7.7 grams of sulphocarbanilide were heated upon an oil-bath to 170–175°. This mixture at first melted, resolidified and remelted with the evolution of carbonic oxysulphide. After heating at 170–175° for ten or fifteen minutes the gas evolution had practically ceased. After cooling, the product was

washed with cold alcohol and practically pure phthalanil was obtained. The yield was 93 per cent.

Phthalanil crystallizes from alcohol in long slender prisms and melts at 204°. Laurent and Gerhardt * give its melting-point at 203°, and Döbner as 205°.†

The first alcoholic washings contain aniline in considerable amount. Upon analysis, phthalanil gave the following results:

0.2464 gram substance gave 0.6790 gram CO_2 and 0.0952 gram H_2O.

	Calculated for $C_{14}H_9O_2N$.	Found.
C	75.34	75.16
H	4.04	4.29

Phthalanil is formed in two ways in this reaction, one of which doubtless depends upon the formation of an unstable diphenylthiophthaluric acid, which breaks down at the temperature of the reaction, as follows:

$$C_6H_4\begin{cases}CONC_6H_5CSNHC_6H_5\\COOH\end{cases} = C_6H_4\begin{cases}CO\\CO\end{cases}NC_6H_5 + COS + C_6H_5NH_2.$$

The second reaction in which phthalanil is formed depends upon the production of phthalanilic acid by the action of the phthalic anhydride on sulphocarbanilide. The phthalanilic acid so formed breaks down, upon heating, into phthalanil and water.

$$C_6H_4\begin{cases}CONHC_6H_5\\COOH\end{cases} = C_6H_4\begin{cases}CO\\CO\end{cases}NC_6H_5 + H_2O.$$

The phthalanil seems to be formed mostly according to the equation in which carbonic oxysulphide and aniline are by-products.

Laurent and Gerhardt‡ first obtained phthalanilic acid by

* Jsb., 1847–48, 605. † Ann. Chem. (Liebig), ccx, 267.

‡ Jsb., 1847–48, 605.

the action of ammonia on phthalanil. They give its melting-point at 192°, at which temperature phthalanil is formed. Zincke and Cooksey * obtained phthalanilic acid by the action of alkalies on phthalanil. They found its melting-point to be 158°, at which temperature the phthalanilic acid decomposed with the formation of phthalanil.

Recently, F. Thorp † obtained phthalanilic acid by the action of hydroxylamine upon orthobenzoylbenzoic acid. Thorp also gives its melting-point as 191–193°, at which temperature he too finds that phthalanilic acid is converted into phthalanil. Phthalanilic acid made by the interaction of phthalic anhydride and sulphocarbanilide, has, according to my observation, a melting-point of 169–169.5°, at which temperature water vapor is given off, the contents of the melting-point tube resolidifying and remelting at 204°, the melting-point of phthalanil.

I have repeated the work of Laurent and Gerhardt, and the melting-point of phthalanilic acid, prepared according to this method, I find not to be 192° but 169–169.5°. Phthalanilic acid was also prepared according to Anschütz's ‡ method, by dissolving molecular quantities of aniline and phthalic anhydride in dry chloroform and allowing the mixture to stand, phthalanilic acid separating in a short time from this solution. Prepared according to this method, I find that phthalanilic acid has the melting-point 169–169.5°.

Action of Sulphocarbanilide on Succinic Anhydride.

Succinanil. — Five grams of succinic anhydride and 11.4 grams of sulphocarbanilide (equal molecules) were heated in an oil-bath until the bath registered a temperature of 150–155°. The contents of the flask liquefied, and a regular evolution of carbonic oxysulphide took place. After heating at this temperature for 30 to 35 minutes, the contents of the flask had become practically solid. This solid product was then washed with cold alcohol to free it from the aniline

* Ann. Chem. (Liebig), cclv, 375. † Ber. Dtsch. chem. Ges., xxvi, 1262.
‡ Ber. Dtsch. chem. Ges., xx, 20, 3214.

which was formed as a by-product. It was then heated with boiling alcohol, and the difficultly soluble portion filtered off. Upon cooling, succinanil separated from the filtrate. A yield of 90 per cent of succinanil was obtained. The difficultly soluble portion had a melting-point of 226°. When pure, the succinanil melted at 150°, which agrees with the melting-point obtained by Hübner.* Upon analysis it gave the following results:

0.2043 gram substance gave 0.5156 gram CO_2 and 0.1031 gram H_2O.

	Calculated for $C_{10}H_9O_2N$.	Found.
C	68.58	68.84
H	5.14	5.60

When succinic anhydride and sulphocarbanilide react at 130–135°, succinanil and the compound melting at 226° are formed, phenyl mustard oil being formed at the same time. At this temperature, the yield of succinanil was small. If, however, the reaction is carried on at 150–155°, succinanil, carbonic oxysulphide, and aniline are practically the sole products. The formation of succinanil at this temperature is doubtless parallel to the formation of phthalanil from phthalic anhydride and sulphocarbanilide. The formation of succinanil may be explained by the following equations:

$$\begin{matrix} CH_2-CO \\ | \quad >O + NHC_6H_5CSNHC_6H_5 = \\ CH_2-CO \end{matrix} \qquad \begin{matrix} CH_2-CONC_6H_5CSNHC_6H_5 \\ | \\ CH_2-COOH \end{matrix}.$$

$$\begin{matrix} CH_2-CONC_6H_5CSNHC_6H_5 \\ | \\ CH_2COOH \end{matrix} = \begin{matrix} CH_2-CO \\ | \quad >NC_6H_5 + COS + \\ CH_2-CO \end{matrix} \qquad C_6H_5NH_2.$$

Succinanilic acid has not as yet been isolated, and I have been as yet unable to identify the compound melting at 226°.

I shall study further the action of urea, sulphourea, sulphocarbanilide, and other substituted ureas upon acid anhydrides.

* Ann. Chem. (Liebig), ccix, 373.

LII

THE GRAVIMETRIC DETERMINATION OF SELENIUM.

By A. W. PEIRCE.*

THE method generally in use for the gravimetric determination of selenious acid is to precipitate the selenium with sulphurous acid in presence of hydrochloric acid and to weigh the elementary selenium. Precipitation by this method, however, is slow and incomplete in many cases, so that it is always necessary to treat the filtrate a second time with sulphurous acid and to digest for some time. To obviate the necessary delay in this process, I have tried the effect of substituting potassium iodide as the reducer instead of the sulphurous acid, adopting the idea from several recent volumetric methods for the determination of selenium† in which an iodide in acid solution is used to reduce the selenious acid, and in which the liberated iodine, caught in various ways, is titrated and taken as a measure of the selenium.

Varying amounts of selenium dioxide prepared according to the method described in former articles, by dissolving pure selenium in nitric acid, removing any selenic acid formed by barium hydroxide, and subliming in a current of dry oxygen, were dissolved in Erlenmeyer flasks, and the solution was acidified with hydrochloric acid. Potassium iodide was added and the selenium was precipitated in the form of a red powder. Boiling for ten minutes served to remove most

* From Am. Jour. Sci., i, 416.

† Muthman and Schaefer, Ber. Dtsch. chem. Ges., xxvi, 1008; Gooch and Reynolds, Am. Jour. Sci., l, 254; Gooch and Peirce, Am. Jour. Sci., fourth series, i, 31. This volume, pp. 338, 348.

of the liberated iodine and to change the selenium into the black modification, which was collected upon an asbestos felt, washed, dried at 100° to a constant weight and weighed. Early experiments showed that for small amounts the process gave accurate results, but that for large amounts the errors came far too high:

Exp.	Se taken.	Se found.	KI.	Volume.	Error.
	grm.	grm.	grm.	cm^3	grm.
(1)	0.0355	0.0356	1	100	0.0001+
(2)	0.0355	0.0355	1	100	0.0000
(3)	0.0355	0.0356	1	100	0.0001+
(4)	0.2968	0.3883	4	75	0.0915+
(5)	0.2033	0.2475	4	100	0.0442+
(6)	0.3058	0.3495	10	100	0.0437+

When the selenium amounted to less than a tenth of a gram the results came out well. When the amount was larger the selenium assumed on boiling a pasty molten condition which made filtering and washing impossible. This condition was observed in the work already referred to, and the mass seemed to consist of selenium with included iodine, as it gave up iodine slowly to water on standing and more rapidly to a solution of potassium iodide.

It has been found in the work to be described that if an excess of potassium iodide be used considerably above the amount necessary for precipitation, the pasty condition of the selenium does not occur, the iodine evidently being held in solution by the excess of the potassium iodide. This would seem to indicate the total release of the iodine, and would make possible the determination of quantities larger than the two-tenths of a gram set in the former work as a limit for the range of the process. Several determinations, which resulted very satisfactorily, were made according to the volumetric method thus modified, and at the same time the selenium which was precipitated was weighed. By the former method, in which the iodine evolved was estimated, the results were too low, and by the latter method, in which

the residue was weighed, too high; but there appeared to be no definite relation between the errors of the two processes, as there would be if the retention of iodine were the only difficulty. Digestion of the selenium in the crucible with hot water removed a small amount of potassium iodide and reduced the error considerably; so that it was apparent that the increase in weight was due to the fact that the precipitated selenium included potassium iodide from the concentrated solution.

Exp.	SeO_2 taken.	SeO_2 found.	KI.	Volume.	Error.	Se taken as SeO_2.	Se found.	Error.
	grm.	grm.	grm.	cm^3	grm.	grm.	grm.	grm.
(7)	0.4870	0.4868	7	60	0.0002–	0.3467	0.3507	0.0040+
(8)	0.4980	0.4971	10	60	0.0009–	0.3545	0.3575	0.0030+
(9)	0.7323	0.7310	10	75	0.0013–	0.5214	0.5312	0.0098+

Later experiments under similar conditions, excepting that the volume of the liquid in which the precipitation took place was very much increased, so that the tendency on the part of the selenium to include the iodide might be diminished, gave errors entirely within satisfactory limits though always positive.

Exp.	Se taken as SeO_2.	Se found.	KI.	Volume.	Error.
	grm.	grm.	grm.	cm^3	grm.
(10)	0.2853	0.2861	7	900	0.0008+
(11)	0.3189	0.3192	8	400	0.0003+
(12)	0.3318	0.3324	7	500	0.0006+
(13)	0.3798	0.3805	7	500	0.0007+
(14)	0.4252	0.4259	7	350	0.0007+
(15)	0.4430	0.4434	10	450	0.0004+

It is sufficient to dilute to 400 cm^3 before acidifying with hydrochloric acid and adding potassium iodide to an amount about three grams in excess of that actually required. Boiling for 10 to 20 minutes will change the selenium to the black modification and remove most of the iodine. The process of precipitation and filtering can be completed in

half an hour. The selenium is dried at 100° to a constant weight.

When the selenium occurs in the higher form of oxidation the reduction follows the same course, though iodine is not liberated until the solution is quite warm; but at the end of the usual time of boiling the action is complete. The following shows the results obtained by acting in the manner described on selenic acid.

SeO_2 taken.	Se taken.	Se found.	KI.	Volume.	Error.
grm.	grm.	grm.	grm.	cm^3	grm.
0.1709	0.1063	0.1065	5	500	0.0002+
0.1709	0.1063	0.1062	5	375	0.0001−
0.3231	0.2010	0.2017	5	350	0.0007+
0.5005	0.3115	0.3126	6	500	0.0011+

Evidently this method will not distinguish between selenious and selenic acids, but it will be found of much value in point of time saved in the determination of either separately, or of the total selenium in case both occur together.

taken to feed the air, which took the place in the bottle of the hydroxide removed, through potash bulbs to prevent the introduction of atmospheric carbon dioxide. The solution of barium hydroxide was standardized by drawing 80 — 90 cm^3 of decinormal iodine into a glass flask, provided with a ground-glass stopper carrying an inlet tube reaching nearly to the bottom of the flask and an outlet tube to which was sealed a Will and Varrentrapp absorption apparatus, and then introducing an appropriate amount of the barium hydroxide solution either from a burette or from a stoppered funnel which was weighed before and after. An ether wash bottle answers admirably for a standardizing flask, and with the glass stopper and its attachments, replaced by a rubber stopper, answers the purpose of the absorption flask described later. The glass stopper is introduced, the inlet being closed by a rubber cap, and the absorption apparatus is charged with a solution of potassium iodide, to hinder the escape of iodine. The solution was brought to a boil, then cooled and the excess of iodine determined by decinormal arsenious acid. It is assumed that the iodine lost acted on barium hydroxide according to the equation

$$6BaO_2H_2 + 6I_2 = Ba(IO_3)_2 + 5BaI_2 + 6H_2O$$

It was found necessary to boil the solution because of the formation of traces of the hypoiodite, which is broken up into iodide and iodate only by boiling, but which, if left unchanged, acts subsequently on the arsenious acid used in titrating the free iodine.

The apparatus which I have found most convenient for evolving the carbon dioxide from the carbonate consisted of a wide-mouthed flask of about 75 cm^3 capacity, furnished with a doubly perforated stopper carrying a separating funnel for the introduction of acid into the flask, and a tube of 0.7 cm. internal diameter, which is expanded to a small bulb just above the stopper, to carry off the gas. This exit tube was joined by a rubber connector to a tube which passed through the rubber stopper, closing the absorption flask (the ether

wash bottle used in standardizing the barium hydroxide solution described above), and which ended in a valve preferably of the Kreider pattern.* This valve was inclosed in a larger tube reaching nearly to the bottom of the absorption flask. Through a second hole in the stopper of the absorption flask passed a glass tube closed by a rubber connector and screw pinch cock.

In making a determination of carbon dioxide, the carbonate was introduced in weighed portions into the boiling flask. Barium hydroxide solution, in amount from 7 — 10 cm^3 more than actually necessary to precipitate the carbon dioxide, was drawn into the absorption flask, which was then connected with the boiling flask as described above. The stop-cock of the separating funnel was shut off and the flasks evacuated by connecting the exit tube of the absorption flask with a filter flask previously pumped out by the water pump, a mercury manometer registering the pressure. Exhaustion to a pressure of from 250–300 mm. was found sufficient and easily attainable with the available water pressure in a minute's time. Sufficient phosphoric acid (chosen as a non-volatile acid) to dissolve the carbonate was introduced into the stoppered funnel with about 50 cm^3 of water, which had been previously purified from carbon dioxide by boiling until one-third had been driven off in steam, and kept in full, stoppered flasks until used. The acid was then allowed to enter the boiling flask and the carbon dioxide driven over completely to the absorption flask by boiling for five minutes — the latter being shaken frequently during the passage of the gas into it and kept cool by standing in a dish of water. The atmospheric pressure was then restored by admitting purified air through the funnel of the boiling flask. In the experiments of Table I, the inlet tube of the absorption flask was closed by a rubber cap after disconnection, the exit tube was attached to potash bulbs and the flask was cooled in a stream of water. The exit tube was removed, a capillary tube long enough to reach below the surface of the liquid introduced and decinormal iodine run

* Loc. cit.

in until the large excess of barium hydroxide had been destroyed. Then the glass stopper of the absorption flask was introduced, with a rubber cap on the inlet tube and potassium iodide solution in the trap, as in standardizing, and the emulsion brought to a boil. Iodine was again run into the hot solution through the inlet tube until the color remained distinctly red after a second boiling. After cooling, the excess of iodine was determined by standard arsenious acid.

TABLE I.

Exp.	$CaCO_3$ taken.	BaO_2H_2 taken.	BaO_2H_2 found.	CO_2 found.	Error on CO_2	Error Corrected.
	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.0501	0.2484	0.1604	0.0227	0.0006+	0.0007+
(2)	0.0500	0.2381	0.1508	0.0224	0.0004+	0.0005+
(3)	0.1022	0.3416	0.1675	0.0447	0.0003−	0.0001−
(4)	0.1026	0.3105	0.1351	0.0450	0.0001−	0.0000
(5)	0.2032	0.6181	0.2692	0.0896	0.0002+	0.0004+
(6)	0.2049	0.5761	0.2223	0.0908	0.0006+	0.0008+
(7)	0.5088	1.1301	0.2606	0.2232	0.0007−	0.0000
(8)	0.5015	1.0804	0.2245	0.2197	0.0010−	0.0003−
(9)	1.0032	2.0125	0.3004	0.4394	0.0020−	0.0006−
(10)	1.0064	2.0702	0.3538	0.4405	0.0023−	0.0009−

In experiments 7, 8 and 9, the barium hydroxide solution was estimated by weight — in the others by volume. The calcium carbonate used was Iceland spar in the form of chips, but, though it was the best material available and considerably better than the best commercial calcium carbonate at hand, the test of drying below red heat and the igniting to the condition of caustic lime with a blow-pipe, proved it to be slightly deficient in carbon dioxide. The observed correction of .0014 grm. for each gram of the carbonate is applied in the last column of the table.

The low results of the larger amounts of carbon dioxide, in contrast to the higher results of the smaller amounts, point to some action of the iodine upon the precipitated carbonate. It would be natural to suppose that such action would be greater upon the carbonate precipitated from a cold solution, and this proved to be the case. For when barium carbonate.

precipitated under the conditions of the analysis described, was treated with 10 cm³ of iodine and boiled again, a loss of 0.0044 grm. of iodine (corresponding to 0.0008 grm. of dioxide) was found; but when barium carbonate was prepared by passing carbon dioxide through a cold solution of barium hydroxide until the presence of the acid carbonate was proved in solution by filtering a portion and boiling — thus insuring the complete destruction of the hydroxide — the precipitated carbonate, after filtering and washing, was acted upon by 10 cm³ of iodine solution to such an extent that 0.0253 grm. of iodine (corresponding to 0.0044 grm. of carbon dioxide) disappeared. The obvious inference is, therefore, that the carbonate should be boiled before the addition of iodine in the process.

TABLE II.

Exp.	$CaCO_3$ taken.	BaO_2H_2 taken.	BaO_2H_2 found.	CO_2 found.	Error on CO_2	Corrected Error.
	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.5023	1.1385	0.2851	0.2190	0.0020—	0.0000
(2)	0.5056	1.1414	0.2801	0.2211	0.0014—	0.0006+
(3)	1.0011	2.0712	0.3704	0.4367	0.0038—	0.0002+
(4)	1.0030	1.8788	0.1736	0.4376	0.0037—	0.0003+

The experiments of Table II were made like those of Table I, excepting in the following points: first, an ordinary flask of about 300 cm³ capacity, which fitted with a rubber stopper, was substituted for the more expensive ground stoppered absorption flask; secondly, the precipitated carbonate was boiled before adding any iodine; and thirdly, after iodine was added to a yellow color and boiled, a second amount of iodine was run in to a red color, but the mixture was not boiled again. By this treatment the iodine is kept from acting on the precipitated carbonate, at least to such an extent that the action is not appreciable, and from attacking the rubber stopper used; incidentally, it is kept from entering the trap, but one is used, nevertheless, to prevent contamination from the outside air. A separating funnel, reaching below the

surface of the liquid, was found a convenient means of introducing the iodine without loss into the hot solution. A higher vacuum is required when the smaller flask is used, especially when large amounts of carbon dioxide are to be determined. A pressure of 200 mm. of mercury was found to be sufficiently low, and in no case did a flask of ordinary thickness and of 300 cm^3 capacity collapse at that degree of exhaustion.

The calcium carbonate used in this test of the smaller apparatus was the purest commercial article available; the error applied as a correction in the last column (0.0040 grm. on carbon dioxide for a gram of carbonate) was determined by five closely agreeing analyses of various amounts in the larger apparatus.

The process, besides being delicate, is fairly rapid — the average time for a determination being about three-quarters of an hour.

LIV

THE IODOMETRIC ESTIMATION OF MOLYBDIC ACID.

By F. A. GOOCH and CHARLOTTE FAIRBANKS.*

I. *The Digestion Method.* — Mauro and Danesi have shown† that under carefully regulated conditions, hydrochloric acid, potassium iodide and a soluble molybdate interact so definitely that the iodine set free from an excess of potassium iodide may be taken as a measure of the molybdic acid, assuming that every molecule of molybdic acid sets free an atom of iodine. They explain this action by the equation:

$$2MoO_3 + 4HI = 2MoO_2I + I_2 + 2H_2O.$$

These results are obtained by acting upon a soluble molybdate containing from 0.1 to 0.5 grm. of molybdic acid with 1.5 grm. of potassium iodide in 1.5 cm^3 of water and 2.5 cm^3 of strong hydrochloric acid, in an atmosphere of carbon dioxide, the whole being heated an hour and a half in a sealed tube. The authors point out that with prolonged heating the action proceeds a little farther, and in the cold, under conditions otherwise similar, not quite so far as the theory of the equation would indicate.

Upon following out exactly the directions of Mauro and Danesi we obtained results similar in general to theirs. The digestion in sealed tubes under the conditions indicated gave results closely comparable with theirs, and these were in fairly good accord with the theory of the reduction. Our results obtained by digesting in the cold and in small volumes for a long time, according to the second method of Mauro and Danesi, were not equally favorable, and these results, as well as those

* From Am. Jour. Sci., ii, 156. † Zeitschr. anal. Chem., xx, 507.

Treatment in Sealed Tubes at 100° for 1½ Hours.
(Method of Mauro and Danesi.)

HCl	H_2O.	KI.	MoO_3, as ammonium molybdate.	MoO_3 found.	Error.
c.c.	c.c.	grm.	grm.	grm.	grm.
2.5	1.5	1.5	0.1010	0.1007	0.0003—
2.5	1.5	1.5	0.3015	0.3008	0.0007—
2.5	1.5	1.5	0.5006	0.4775	0.0031—
2.5	1.5	1.5	0.5020	0.4924	0.0096—

Treatment 18–22 Hours in Cold.
(Method of Mauro and Danesi.)

HCl.	H_2O.	KI.	MoO_3 as above.	MoO_3 found.	Error.
c.c.	c.c.	grm.	grm.	grm.	grm.
2.5	1.5	1.5	0.0986	0.0982	0.0004—
2.5	1.5	1.5	0.0982	0.0979	0.0003—
2.5	1.5	1.5	0.2041	0.2024	0.0017—
2.5	1.5	1.5	0.2059	0.2043	0.0016—
2.5	1.5	1.5	0.2068	0.2040	0.0028—
2.5	1.5	1.5	0.3116	0.3059	0.0057—
2.5	1.5	1.5	0.3098	0.3011	0.0087—
2.5	1.5	1.5	0.4080	0.4011	0.0069—
2.5	1.5	1.5	0.4087	0.4015	0.0072—
2.5	1.5	1.5	0.5210	0.5102	0.0108—
2.2	1.5	1.5	0.5172	0.5023	0.0149—

Treatment at 100° for 1 Hour.
(Amounts of liquid and iodide different from those of Mauro and Danesi.)

HCl.	H_2O.	KI.	MoO_3 taken.	MoO_3 found.	Error.
c.c.	c.c.	grm.	grm.	grm.	grm.
15	15	0.5	0.0893	0.0897	0.0004+
15	15	0.5	0.0824	0.0813	0.0011—
15	15	0.5	0.0828	0.0813	0.0015—
15	15	0.5	0.0990	0.0982	0.0008—
10	10	0.5	0.0841	0.0842	0.0001+
10	10	0.5	0.1683	0.1591	0.0092—
10	10	0.5	0.1706	0.1536	0.0170—
20	20	0.5	0.1695	0.1638	0.0062—

Treatment 18 Hours in Cold.
(Amounts of liquid different from those of Mauro and Danesi.)

HCl.	H_2O.	KI.	MoO_3 taken.	MoO_3 found.	Error.
c.c.	c.c.	grm.	grm.	grm.	grm.
40	10	1.5	0.5018	0.4847	0.0171—
90	30	1.5	0.5005	0.4910	0.0095—
75	25	1.5	0.5035	0.4934	0.0101—
75	25	1.5	0.5022	0.4920	0.0102—

obtained by varying the treatment, indicated an increasing difficulty in the reduction of the molybdic acid as its amount increased. As will be seen from the table, the method of Mauro and Danesi was varied in two ways: instead of only treating in small volumes (4 cm^3) at 100° C., we used larger volumes (20 cm^3 to 30 cm^3) at 100° C. with weaker acid and smaller amounts of the iodide; and instead of the treatment in the cold of only small volumes (4 cm^3), large volumes (50 cm^3 to 100 cm^3 with stronger acid were used.

The explanation of these experimental results we were inclined to believe lay in a tendency on the part of the iodine, set free in the process, to reverse the action. If this is so, the obvious remedy should be found in the removal of the iodine from the sphere of action, and this idea led us to experiment upon a process of distillation in which the iodine should be collected and estimated in the distillate; but before our work was completed, Friedheim and Euler published* the results of their investigation along the same line.

II. *Distillation Process.* — These investigators have shown that if molybdic acid is treated with potassium iodide and hydrochloric acid, one atom of iodine is distilled for every molecule of molybdic acid present. The process according to their directions consists in treating in the Bunsen apparatus from 0.2 to 0.3 grm. of a soluble molybdate, or molybdic acid dissolved in sodium hydroxide, with 0.5 grm. to 0.75 grm. of potassium iodide and enough hydrochloric acid (sp. gr. 1.12) to two-thirds fill the flask. The solution is warmed for some time and only heated to boiling when the flask is wholly filled with the heavy vapor of iodine. It is boiled until no more iodine is visible and the liquid is of a clear green color. The iodine, collected in a receiver previously charged with a solution of potassium iodide, is then titrated with a standard thiosulphate solution. Results, varying between 0.03 per cent and 1.1 per cent on amounts, ranging from 0.2 grm. to 0.4 grm., of the molybdic acid present, were obtained by them.

Our experience fully confirms the usefulness of the method

* Ber. Dtsch. chem. Ges., xxviii, 2066.

of Friedheim and Euler, but we have found it necessary to define more exactly the conditions of distillation. It is not sufficient to say that the boiling shall be stopped when a clear green color appears and when the steam is no longer colored by iodine; for the green color comes very gradually and we have repeatedly found iodine in the residue after the green color had developed distinctly. We have found it safer and more convenient to start the distillation with a definite volume of liquid and boil until the volume is reduced to a definite point.

Our work has shown that if the initial volume is about 40 cm^3 no iodine remains in the flask after the liquid has been boiled down to 25 cm^3 and that at that degree of concentration the molybdic acid shows the theoretical reduction; but if the concentration is pushed beyond this point, a tendency to further reduction of the molybdic acid becomes evident.

We find it necessary to carry on the distillation in an atmosphere of carbon dioxide, inasmuch as the hydriodic acid freed by the action of hydrochloric acid of the strength employed upon the potassium iodide, is decomposed by distillation in contact with air, with liberation of iodine. As even a trace of oxygen will immediately set free iodine from boiling hydriodic acid, the carbon dioxide must be as free as possible from oxygen. The carbon dioxide which we used was evolved from boiled marble by the action of boiled acid to which a little cuprous chloride had been added, and was finally passed through a solution of iodine in potassium iodide to free it from any reducing substance which might be present.

FIG. 15.

The apparatus which we found most satisfactory was constructed with sealed and ground joints exclusively, and is shown in the accompanying figure. The distillation takes place in the first flask, and the iodine collects in the second flask and trap, which

hold a solution of potassium iodide kept cool by immersion of the flask in cold water.

Before making the test experiments, a stream of the purified carbon dioxide was passed through the whole apparatus for some minutes and the stopcock in the funnel was closed.

Ammonium molybdate, from 0.1 to 0.4 grm., dissolved in 10 cm^3 of boiled water, was put in the stoppered funnel and almost all of it allowed to run into the first flask. It was necessary that a few drops be left in the funnel or the liquid to follow would carry down bubbles of air. This precaution is necessary to the attainment of good results. Ten cubic centimeters of boiled water containing 0.5 grm. of potassium iodide were introduced similarly, and finally 20 cm^3 of strong hydrochloric acid (sp. gr. 1.20). Before the acid was allowed to run in wholly, the stoppered funnel was again filled with carbon dioxide and finally left connected with the generator so that carbon dioxide might be passed into the apparatus at any time.

The liquid in the first flask, which at that time held the ammonium molybdate, 0.5 grm. of potassium iodide, 20 cm^3 boiled water and 20 cm^3 of hydrochloric acid (sp. gr. 1.20), was boiled until the volume decreased to 25 cm^3. Under these conditions we do not find it necessary to digest the mixture before boiling. The iodine in the second and third flasks was titrated with standard thiosulphate.

The ammonium molybdate which we used in all the experiments was prepared by twice recrystallizing presumably pure molybdate. This salt was proved to contain 81.55 per cent of molybdic acid by the fact that a given weight of the molybdate was found to liberate 81.55 per cent of the amount of iodine set free by the same weight of pure molybdic anhydride dissolved in sodium hydroxide and treated similarly.

We have found it to be a matter of importance that the potassium iodide present shall never exceed the theoretical requirement by more than half a gram; otherwise the reducing action on the molybdic acid will be forced too far. When the amount of molybdic acid present is less than 0.3 grm.

it is safer to restrict the potassium iodide used to half a gram.

MoO_3 as ammonium molybdate taken.	KI.	MoO_3 found.	Error.
grm.	grm.	grm.	grm.
0.2585	0.5	0.2580	0.0005−
0.2995	0.5	0.2991	0.0004−
0.2524	0.5	0.2513	0.0011−
0.2446	0.5	0.2457	0.0011+
0.2903	0.5	0.2914	0.0011+
0.2798	0.5	0.2808	0.0010+
0.2656	0.5	0.2663	0.0007+

MoO_3 dissolved in NaOH.	KI.	MoO_3 found.	Error.
grm.	grm.	grm.	grm.
0.2273	0.5	0.2281	0.0008+
0.2052	0.5	0.2062	0.0010+
0.3474	0.5	0.3467	0.0007−

III. *Reoxidation Process.* — It was noticed during our experiments upon the method of Mauro and Danesi, as has been remarked previously, that large amounts of iodine in the digestion flask seemed to react upon the reduced product. In the process of Friedheim and Euler, too, it was discovered that, when the iodine which had collected in the second flask was drawn back into the first flask and mixed with the hot reduced product, the iodine found by titration was deficient in amount. It was found also that small amounts of standard iodine, introduced into the flask containing the reduced molybdic acid in an atmosphere of carbon dioxide, were absorbed slowly when this mixture was heated. This slow disappearance of the iodine in acid solution suggested the possibility of effecting the complete oxidation of the reduced molybdic acid in an alkaline solution, containing a tartrate or other salt of an organic acid to prevent precipitation. Several experiments were made in this direction upon the residues left in the process of Friedheim and Euler, the distillate having

been titrated as usual with sodium thiosulphate to make sure that the reduction had proceeded properly. These residues were treated in each case with 1 grm. of tartaric acid, neutralized by acid sodium carbonate and left standing for an hour or two with an excess of standard iodine. Upon determining, by means of standard arsenious acid, the iodine left over, it was found that the amount of it which had disappeared corresponded very closely with that set free in the distillation, which is of course the same as that necessary to reoxidize the molybdic acid completely.

The conditions necessary to complete oxidation being known, experiments were made to see whether the process could not be successfully carried on in an open flask. Naturally under these conditions the air present must, as in the previous experiments, tend to set free some iodine at the outset, but, inasmuch as the hydriodic acid gradually diminishes in strength as the molybdenum is reduced and all iodine is ultimately driven from the flask, which is filled with steam during the boiling, it seemed possible that the danger from the action of atmospheric oxygen might be so far reduced as not to interfere essentially in the estimation of the molybdenum in the residue, provided the contents of the flask is diluted and cooled at the end of the boiling. Ammonium molybdate containing from 0.1 to 0.3 grm. molybdic acid, 0.5 grm. of potassium iodide, 20 cm^3 of water and 20 cm^3 of hydrochloric acid (sp. gr. 1.20) — the same proportions as those used in the process of Friedheim and Euler — were put into a 100 cm^3 flask or narrow-based Erlenmeyer, and boiled from a total volume of 40 cm^3 to exactly 25 cm^3, a point carefully marked on the flask. At this point of concentration, tests, repeated in many cases, have shown no free iodine in the reduced solution. If the solution is boiled below 25 cm^3, there is a tendency for the reducing action to go too far.

The residue was diluted at once, neutralized with acid sodium carbonate, and treated with an excess of standard iodine.

For a trap to prevent loss during boiling, a two-bulbed

calcium chloride tube, cut off as shown in the figure four centimeters below the larger bulb, was fitted loosely inside the neck of the flask. Too violent boiling was prevented by the addition of two or three small pieces of pumice stone. While still acid the reduced solution, diluted and containing at this time little hydriodic acid, is not appreciably reoxidized in the air for some time; but when once made alkaline, it is very easily changed. Therefore the iodine for reoxidation must either be added before the solution is made alkaline or great care must be taken while neutralizing to stir the solution as little as possible and to draw in the iodine immediately. Less chance for error is introduced if the reduced solution is put, with an excess amounting to at least 8 cc. of decinormal iodine and with a gram of tartaric acid, to prevent precipitation, in a liter flask, corked and then neutralized with acid sodium carbonate. The flask is fitted with a paraffined rubber stopper, carrying a funnel with a stop-cock for introducing the acid sodium carbonate and a Will and Varrentrapp trap for catching in a solution of potassium iodide any iodine thrown off during the effervescence. In some of the test experiments normal potassium carbonate, as causing less effervescence, was substituted for the acid sodium carbonate during the first part of the neutralization; the solution, however, must always finally be made alkaline with the acid carbonate.

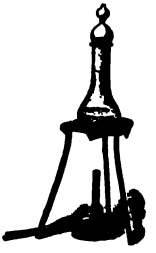


FIG. 16.

The simpler method of neutralization is to put the reduced solution and a gram of tartaric acid in a liter flask, adding enough sodium hydroxide to nearly neutralize the solution, and finally making the solution surely alkaline with acid sodium carbonate. An excess of the standard iodine must be drawn in at once or atmospheric oxidation will take place and the error of the process be great.

If the solution has been properly neutralized according to either method, the iodine color should perceptibly fade within fifteen minutes, but for complete oxidation the trapped or

corked bottle should be set aside out of sunlight for an hour and a half or two hours. The iodine which was not used for reoxidation was then titrated with a standard arsenic solution. Since there is a slight tendency, especially when sodium hydroxide and acid sodium carbonate are used for neutralization, toward the formation of a little iodate, it is wise to acidulate the solution in each case slightly with dilute hydrochloric acid and then to determine by sodium thiosulphate the iodine which has taken the form of iodate. The ratio 126.85 : 144 expresses the relation of the total amount of iodine used in the reoxidation process to the calculated amount of molybdic acid present. The table given below shows the amount of molybdic acid taken in the form of ammonium molybdate and the molybdic acid found calculated from the iodine used in reoxidation.

MoO_3 as ammonium molybdate.	KI.	MoO_3 found.	Error.	Neutralized by
grm.	grm.	grm.	grm.	
0.1640	0.5	0.1639	0.0001−	$K_2CO_3 + NaHCO_3$
0.1692	0.5	0.1681	0.0011−	" "
0.1666	0.5	0.1661	0.0005−	" "
0.1517	0.5	0.1517	0.0000	$NaHCO_3$
0.2530	0.5	0.2537	0.0007+	"
0.1636	0.5	0.1637	0.0001+	"
0.1702	0.5	0.1702	0.0000	"
0.1520	0.5	0.1518	0.0002−	"
0.1642	0.5	0.1652	0.0010+	"
0.4560	0.75	0.4560	0.0000	"
0.1690	0.5	0.1683	0.0007−	$NaOH + NaHCO_3$
0.0507	0.5	0.0519	0.0012+	" "
0.1663	0.5	0.1666	0.0003+	" "
0.0101	0.5	0.0095	0.0006−	" "
0.1639	0.5	0.1632	0.0007−	" "
0.1636	0.5	0.1625	0.0011−	" "
0.0507	0.5	0.0510	0.0003+	" "
0.1685	0.5	0.1683	0.0002−	" "
0.1514	0.5	0.1512	0.0002−	" "
0.1649	0.5	0.1646	0.0003−	" "
Average error in the experiments, −0.0001 gram.				

The results given in the foregoing table show that molybdic acid can be determined with accuracy and convenience

by boiling it with hydrochloric acid and a small excess of potassium iodide to a definite concentration in an ordinary flask, then neutralizing the residue with acid sodium carbonate, and reoxidizing the reduced molybdic acid with standard iodine.

LV

ON THE EXISTENCE OF SELENIUM MONOXIDE.

By A. W. PEIRCE.*

It was Berzelius's idea that the odor of decayed cabbage which is noticed when selenium is burned in air is due to the formation of a gaseous lower oxide of selenium which he called the monoxide. The same oxide is said to be formed when selenium sulphide is dissolved in an insufficient amount of aqua regia, in the distillation of a mixture of selenium and selenium dioxide, and in the action of sulphur upon selenium dioxide.

Sacc † records his inability to obtain such an oxide, and attributes the odor which is noticed under these conditions to a trace of selenium hydride. A very minute trace of the hydride is sufficient to develop a very considerable odor, and traces of moisture may be enough to produce a perceptible odor of the hydride when the conditions are favorable to action upon the elementary selenium. When selenium burns in air, or when its sulphide is oxidized by aqua regia, moisture is inevitably present, and when selenium dioxide is reduced by sulphur or intermixed with elementary selenium its extremely hygroscopic character implies the presence of traces of water.

It has been a generally accepted opinion of late that the selenium monoxide does not exist, but more recently, in work upon certain organic compounds of selenium, Chabrié has been led to the idea that the monoxide does exist and that it is a solid body. Chabrié states ‡ that when selenium is heated in air it tends to increase in weight. At 100° C. the

* From Am. Jour. Sci., ii, 163. † Ann. Chim. III, xxi, 119.
‡ Ann. Chim., VI, xx, 273.

increase is said to be inappreciable, but at 180° C. it approaches very nearly to the limit corresponding to the formation of the selenium monoxide, SeO. Further he says that this increase in weight when the selenium is heated to 180° cannot be due to the formation of the dioxide, since that compound, if it were formed, could be seen as a crystalline deposit; or if the temperature is too high to allow it to deposit, a loss of weight would result. He is so sure of the increase that, were it not for the fact that the monoxide has not been generally recognized, he would suggest as a possible means for the determination of selenium to heat it to 180° and estimate it as SeO. The selenium with which Chabrié obtained these results was reduced by acting with sodium sulphite and hydrochloric acid upon the product of oxidation of certain organic compounds of selenium of the aromatic series by means of nitric acid, and filtering on glass wool. The product when dried quickly at 100° gave results in accord with his theory of the constitution of the compounds, counting the selenium dried at 100° as existing in elementary form. Thus:

	I.	II.	III.
Se found	0.0347	0.0680	0.0406
Se by theory	0.0349	0.0678	0.0414
	0.0002—	0.0002+	0.0008—

In other analyses of the same compounds, in which the selenium was dried at 180° instead of at 100°, the weight of the selenium was so much greater as to suggest the idea that the element had oxidized to the condition of the monoxide.

Thus:

	I.	II.	III.	IV.
SeO (?) found	0.0301	0.0525	0.0523	0.0517
SeO by theory	0.0301	0.0517	0.0504	0.0498
	0.0000	0.0008+	0.0019+	0.0019+

Had Chabrié actually found that the same identical selenium determined by drying to a constant weight at 100°, did actually increase in weight at 180° to a constant amount

corresponding exactly to what the weight should be were the monoxide formed, the evidence of such oxidation would be good. What Chabrié did, however, was to show that when the selenium from one sample of his compound was dried at 100° and regarded as elementary selenium, the amount of it found corresponded to his theory of the composition of his compound; while to harmonize the results of analysis with the demands of the theory, when the selenium from another sample of the same preparation was heated to 180° it became necessary to assume that the selenium had been oxidized to the condition of the monoxide. Moreover, it has been shown very recently by Krafft and Kaschau * that the composition and constitution given by Chabrié to some, at least, of his organic compounds of selenium cannot be sustained. It has seemed to be desirable, therefore, to put the question of the oxidation of selenium at 180° to the direct test.

I have dried selenium to a constant weight at 100° C. and then have heated it to 180° C. for various periods of time, and in no single case have I observed the slightest increase in weight. In the following table are the results of these experiments. In every case the selenium was taken originally as the dioxide, prepared as described in previous articles, and precipitated in some cases with sulphurous acid, in some instances with potassium iodide, dried to a constant weight at 100° and then heated to the temperature and for the periods indicated below:

Exp.	Se found at 100°.	Temperature.	Time.	Weight.	Loss.
	grm.		hours.	grm.	grm.
(1)	0.0356	110°	½	0.0350	0.0006
		180°	½	0.0348	0.0002
(2)	0.0355	110°	½	0.0350	0.0005
		180°	½	0.0347	0.0003
		150°	½	0.0346	0.0001
(3)	0.0576	180°	8½	0.0546	0.0030
(4)	0.0576	180°	8½	0.0558	0.0018
(5)	0.3324	180°	2	0.3306	0.0018
(6)	0.3500	180°	1½	0.3445	0.0055
(7)	0.4274	180°	1½	0.4232	0.0042

* Ber. Dtsch. chem. Ges., xxix, 428.

Other experiments were made for the purpose of determining if possible just how the losses occur. The selenium collected as usual upon asbestos in a perforated crucible was introduced into a large glass tube placed horizontally in an air bath in such manner that the tube extended outside the bath at both sides and remained cool at the ends. A current of dry air was drawn through ignited asbestos and then through the tube containing the selenium and crucible, and passed to the suction pump through a glass trap filled with water. A thermometer placed within the tube and closely adjacent to the selenium showed the temperature of the selenium as the experiment progressed. On gradually heating the bath no change was observed at first, but at 180° C. a mirror of red elementary selenium formed on the cooler portions of the tube outside the bath, but did not extend so far as the trap. At the end of the heating the crucible was weighed and the loss determined. The washings of the tube and the trap when acidified and tested with potassium iodide gave no indication of selenious acid, as would inevitably be the case if selenium dioxide were formed and volatilized during the heating. The loss is due, therefore, entirely to the volatilization of the selenium as such.

Exp.	Se found at 100°.	Temperature.	Time.	Weight.	Loss.
	grm.		hours.	grm.	grm.
(8)	0.0706	180°	2¼	0.0628	0.0078
(9)	0.0987	180°	1¾	0.0948	0.0039*
(10)	0.3192	180°	4	0.3121	0.0071
(11)	0.0983	180°	3¾	0.0925	0.0058
		200°	2	0.0876	0.0049

In every case, irrespective of the reducing agent employed or details of treatment, I get a loss of weight on heating selenium in air to 180°, due to the volatilization of the selenium. If this is so, it should be possible to so arrange the apparatus that the selenium volatilized may be caught and weighed.

* In current of CO_2 instead of air.

A drying tube with ground-in stopper was, therefore, sealed to a smaller tube carrying a bulb filled with ignited asbestos. The selenium was weighed and introduced upon an asbestos felt into the larger tube and the whole was carefully weighed.

The larger tube was heated in the air bath, while air was drawn through the tube in the direction of the bulb of asbestos, which was outside the bath and cool. Selenium volatilized as before, very evidently, as far as the asbestos in the bulb, where it was caught. On cooling and weighing the tube and contents, absolutely no change of weight was observed. This shows that no gaseous product is formed to occasion the loss, but that the decrease of weight in the former experiments was due to the volatilization of the selenium itself.

Thus I am unable to duplicate the results of Chabrié in this matter, although I have followed his method of treatment so far as it is described. The only difference apparent is in the source of the selenium — in this work the dioxide of known purity with which much exact work has recently been done, and in Chabrié's work the oxidation product of certain organic compounds. I fail to see, however, how this difference in origin can affect the sensitiveness of the selenium with reference to the oxidizing action of the air.

Having thus been unable to obtain the monoxide in the solid state, I have made some experiments upon the oxidation of selenium by heating it in mixture with the dioxide under such conditions that the existence of a gaseous product, such as Berzelius describes it to be, would be noted, even if it were formed in very small amount.

A hard glass tube of convenient size, about 2 cm. in diameter and 65 cm. in length, was washed and dried most carefully and sealed at one end. Through the open end were introduced 0.0247 grm. pure selenium dioxide, freshly prepared and scrupulously protected against moisture, and 0.0250 grm. powdered selenium. The open end was then drawn out in such a way that attachment could easily be made to an air

pump and an intervening portion of the tube constricted so as to be easily sealed later. The end was attached to a mercury air pump and the pressure reduced to 4 mm. By applying a flame to the constricted part the tube was sealed in that condition. The tube was heated gradually in a small combustion furnace until the whole contents were vaporized, maintained in that condition some minutes and then cooled. At every opportunity of lower temperature the selenium vapors would condense into dark metallic drops which ran into larger and larger drops, like mercury globules, seeming to separate from the dioxide vapors. This treatment was repeated six times at intervals, the contents of the tube showing each time the same phenomena of sublimation and condensation. Nothing was observable at any time to indicate chemical change in either substance, each maintaining the characteristics of its own sublimation.

Finally the air pump was again attached and allowed to work until the manometer registered no pressure. Upon breaking the end of the tube by pinching it inside the rubber connector, the height of the mercury column indicated the same pressure as when the tube was originally sealed. When disconnected the tube possessed not the slightest odor.

This experiment was repeated with the sole modification that the heating was not carried to a temperature so high, and this time 0.0730 grm. freshly prepared dry selenium dioxide and 0.0730 grm. powdered selenium were sealed up in the evacuated tube and heated for seven hours at 180°C. and finally for one hour at 200°. Upon breaking the tube under conditions similar to those of the previous experiment the contents showed no pressure and possessed no odor. Obviously no gaseous product was formed under these conditions.

I have thus been unable to find evidence of the existence of selenium monoxide, either gaseous or solid, and my experience goes to show that the peculiar smell attributed by Berzelius to the monoxide is only developed, as Sacc found, when selenium is heated in presence of moisture, and that a mere trace of moisture is sufficient to produce the odor.

LVI

AN IODOMETRIC METHOD FOR THE DETERMINATION OF PHOSPHORUS IN IRON.

By CHARLOTTE FAIRBANKS.*

A RECENT paper from this laboratory† showed that molybdic acid was reduced by hydriodic acid to the condition of oxidation represented by the symbol Mo_2O_5 in acid solution, while in an alkaline solution the reduced product was reoxidized by standard iodine.

In acid solution, $2MoO_3 + 2HI = Mo_2O_5 + I_2 + H_2O$.
In alkaline solution, $Mo_2O_5 + I_2 + H_2O = 2MoO_3 + 2HI$.

These reactions obviously present the possibility of developing a method for the determination of phosphorus in the phospho-molybdates.

The very careful work of Blair and Whitfield‡ shows conclusively that the ammonium phospho-molybdate, precipitated under the conditions ordinarily prescribed for the determination of phosphorus in iron or iron ores is of definite constitution. They find that $24MoO_3$, P_2O_5, $3(NH_4)_2O$, $2H_2O$ expresses the composition of this phospho-molybdate, which therefore contains 1.794 parts of phosphorus to every 100 parts of molybdic anhydride.

This being the case, it is plain that if advantage can be taken of the fact that the amount of iodine necessary to reoxidize reduced molybdic acid is large, as well as of the fact that the amount of molybdic acid compared to the phosphorus contained in the phospho-molybdate is also large, a method of great theoretical accuracy should result.

I have experimented with a process which consists essen-

* From Am. Jour. Sci., ii, 181.

† Gooch and Fairbanks, Am. Jour. Sci., ii, 156. This volume, p. 375.

‡ Jour. Amer. Chem. Soc., xvii, 747.

tially in treating the ammonium phospho-molybdate, produced by the accepted methods of iron analysis, with potassium iodide in the presence of strong hydrochloric acid and under carefully regulated conditions; in neutralizing the residue thus obtained by acid sodium carbonate; and in reoxidizing the reduced molybdenum compound to the condition of molybdic acid by titration with iodine.

The directions prescribed by Blair and Whitfield for making the ammonium molybdate solution were followed: 100 grams of molybdic anhydride are intimately mixed with 400 cm^3 of distilled water and 80 cm^3 of strong ammonia, and after filtering this liquid is poured into a mixture of 300 cm^3 of nitric acid (1.42 sp. gr.) and 700 cm^3 of water. This solution, it is said, practically remains unaltered for months; but it is much safer to filter each day the portion to be used.

In order to obtain a standard solution of phosphorus, 1.2 grams of microcosmic salt were dissolved in one liter of water and 50 cm^3 of this solution were evaporated, and the residue ignited and weighed as sodium metaphosphate.

Iron free from phosphorus, for admixture with known amounts of phosphorus in the test experiments, was prepared by igniting ferrous oxalate. The oxalate was precipitated by oxalic acid from ferrous sulphate dissolved in warm water. The precipitate was then thoroughly washed with cold water, dried and ignited.

The ferric oxide thus obtained was dissolved in hydrochloric acid, evaporated to dryness, and dried on a hot plate. The ferric chloride was treated with nitric acid and the solution evaporated twice. In this way all but a trace of the chloride was destroyed.

Since in the ordinary determination of phosphorus in iron, potassium permanganate is added, as Drown says,* to insure the complete oxidation of the phosphorus to the orthophosphoric acid, it seemed best to make sure that this treatment was not detrimental in the process to follow. Enough permanganate was therefore added in my experiments to distinctly

* Trans. Am. Inst. Min. Eng., xviii, 93.

color the already boiling solution of ferric nitrate, and then a little tartaric acid was used to clear the solution.

As too much free acid prevents the full precipitation of the ammonium phospho-molybdate, the ferric nitrate solution was treated with ammonia until a precipitate or the ruby wine color appeared. Then dilute nitric acid was added until the color of the solution was a clear amber. Generally four or five grams of ferric oxide were used in each determination.

The ferric nitrate and phosphorus solutions, in volume not less than 150 cm^3 nor more than 300 cm^3, were drawn into an ordinary 500 cm^3 flask. The flask was heated on the steam bath to just 85° C. — very carefully, since at higher temperatures there is danger of precipitating molybdic acid — and immediately 40 cm^3 of the filtered ammonium molybdate solution were so added as to wash down the thermometer and the sides of the flask. The flask was corked, wrapped in a towel, and shaken for five minutes. The contents were filtered at once on an asbestos felt, and the precipitate washed three or four times, first with a 10 per cent solution of nitric acid, and then with a 1 per cent solution of potassium nitrate.

If the nitric acid and potassium nitrate solutions wash the flask and cork each time, it will do no harm if some of the precipitate still adheres to the sides of the flask; for the flask, cork and crucible are all finally washed with ammonia. The asbestos felt was transferred to a 100 cm^3 flask or narrow based Erlenmeyer. The precipitation flask and cork were thoroughly washed with a mixture of 5 cm^3 of ammonia and ten cm^3 of water, and the washings were allowed to rinse the sides of the perforated crucible — standing on a small funnel — and so to run into the 100 cm^3 flask. Twenty-five cubic centimeters of strong hydrochloric acid were added and, where the phosphorus does not exceed 0.0060 grm., 0.5 grm. of potassium iodide; but, where more than 0.0060 grm. of phosphorus is present, a little more potassium iodide is theoretically and practically needed. Experience has shown that the iodide present should not exceed the amount theoretically necessary by more than a half gram.

The liquid was boiled down from a total volume of 40 cm³ to just 25 cm³, a volume easily marked by two strips of paper pasted on opposite sides of the flask. If the solution is boiled farther, the molybdic acid is likely to be reduced beyond the degree of oxidation indicated by the symbol Mo_2O_5. The residue was neutralized with acid sodium carbonate, according to one or the other of the methods described below, and treated with an excess of standard iodine.

FIG. 16.

For a trap to prevent loss during boiling, a two-bulbed drying tube was cut off an inch and a half below the largest bulb and this end fitted loosely into the neck of the flask, as shown in the accompanying figure. The addition of two or three little pieces of pumice stone, previously boiled in hydrochloric acid, insures quiet boiling.

While still acid the reduced solution is not appreciably reoxidized in the air, but when once made alkaline it is very easily changed. Therefore great care must be taken either to have the iodine present before the solution is made alkaline, or else to stir up the solution as little as possible while adding the alkalies and to draw in the iodine solution immediately.

The safer method is to put the reduced solution, with one gram of tartaric acid, to prevent the precipitation of the molybdenum, and an excess of the iodine solution, amounting to at least 8 cm³ into a liter flask. This flask was fitted with a paraffined rubber stopper, carrying a funnel with a stop-cock for admitting slowly the acid sodium carbonate to effect neutralization, and a Will and Varrentrapp trap, filled with a solution of potassium iodide, to catch the iodine thrown off during the effervescence.

The more convenient way, and after a little practice a serviceable method for rapid work, is to put the solution and the tartaric acid in a bottle, to add enough sodium hydroxide to nearly neutralize the free acid, and then to make the solution distinctly alkaline with an excess of acid sodium

carbonate, tipping the flask to one side to prevent loss during the effervescence. The iodine solution must be drawn in immediately or atmospheric oxidation will take place and the error of the process be great.

After either method of neutralization the iodine color in the solution should perceptibly fade within fifteen minutes; but for complete oxidation the corked bottle should be set aside, out of sunlight, for an hour and a half, and then the excess of the iodine titrated with a standard solution of arsenious acid.

Since there is a slight tendency on the part of the iodine, especially when the sodium hydroxide and the acid sodium carbonate are used for neutralization, to form a little iodate, it is wise to acidulate the solution in each case slightly with dilute hydrochloric acid after the titration with the arsenic solution, and then to determine by sodium thiosulphate the trace of iodine which has taken the form of iodate.

In the following table the absolute errors in terms of phosphorus are given; and the percentage errors, between the phosphorus taken and the phosphorus found, referred to 10 grams of material — the maximum amount of high grade iron or steel usually taken for analysis — are also added.

Exp.	Amount of P taken.	Amount of P found.	Error on P.	Per cent of error of P.	Neutralized by
	grm.	grm.	grm.		
(1)	0.002727	0.002778	0.000051+	0.0005 +	$NaHCO_3$
(2)	0.001812	0.001743	0.000069—	0.0007 —	$NaOH + NaHCO_3$
(3)	0.000909	0.000914	0.000005+	0.00005+	$NaOH + NaHCO_3$
(4)	0.003508	0.003262	0.000246—	0.002 —	$NaOH + NaHCO_3$
(5)	0.005454	0.005417	0.000037—	0.0003 —	$NaHCO_3$
(6)	0.001818	0.001861	0.000043+	0.0004 +	$NaOH + NaHCO_3$
(7)	0.003636	0.003716	0.000080+	0.0008 +	$NaHCO_3$
(8)	0.000909	0.000988	0.000079+	0.0007 +	$NaHCO_3$
(9)	0.000363	0.000289	0.000074—	0.0007 —	$NaOH + NaHCO_3$
(10)	0.008180	0.008179	0.000001—	0.00001—	$NaHCO_3$

The error in (4) is obviously high, and, in view of the results obtained in the former paper to which reference has been made, undoubtedly accidental; but the result is inserted in the series because no reason was apparent for excluding it.

In all of the experiments, with one exception, from four to five grams of pure iron oxide were introduced; in experiment (9) the amount was 2.5 grm.

In the first nine experiments, 0.5 grm. of potassium iodide was used; in experiment (10) more was theoretically necessary and 0.75 grm. was added.

The foregoing table shows that satisfactory results in the determination of phosphorus in iron can be obtained by precipitating the ammonium phospho-molybdate according to the usual methods of iron analysis; then reducing the phospho-molybdate thus obtained with potassium iodide and hydrochloric acid; neutralizing the residue with acid sodium carbonate, and reoxidizing with standard iodine.

LVII

ON THE REDUCTION OF VANADIC ACID BY HYDRIODIC AND HYDROBROMIC ACIDS, AND THE VOLUMETRIC ESTIMATION OF THE SAME BY TITRATION IN ALKALINE SOLUTION WITH IODINE.

By PHILIP E. BROWNING.*

THE reduction of vanadic acid from the condition of the pentoxide to that of the tetroxide by the action of hydriodic and hydrobromic acids has been applied to the volumetric determination of vanadium. Holverscheit† has shown that when a vanadate is treated with potassium bromide and strong hydrochloric acid, and the bromine liberated on boiling is passed into a solution of potassium iodide, the iodine set free and estimated shows the reduction to have gone to the condition of the tetroxide. This method is said to yield most satisfactory results.

Friedheim in a recent paper‡ gives the method favorable comment, and shows also by a carefully made series of experiments that the pentoxide may be reduced to the tetroxide by boiling with potassium iodide and sulphuric acid, and, further, that the reduction may be carried even to the condition of the trioxide by substituting for the sulphuric acid strong hydrochloric acid.

In both of the above mentioned methods the iodine liberated is conducted into a solution of potassium iodide and estimated in the usual manner.

In a former paper§ I have shown that vanadic acid may be determined conveniently and rapidly by reducing it to the

* From Am. Jour. Sci., ii, 185.
† Dissertation, Berlin, 1890.
‡ Ber. Dtsch. chem. Ges., xxviii, 2067.
§ Zeitschr. anorg. Chem., vii, 158.

tetroxide by the action of tartaric acid and estimating it in the residue by direct oxidation with standard iodine after having cooled the solution and having made it alkaline with a bicarbonate. The possibility of applying this method of oxidation to the residue after the reduction with hydrobromic and hydriodic acids led to the series of experiments which it is the purpose of this paper to describe. The advantages of the treatment of the residue are obvious and the general method has been applied in a number of methods previously developed in this laboratory. In the first place the complicated apparatus necessary for the distillation and collection of the bromine or iodine is unnecessary, an ordinary boiling flask or Erlenmeyer beaker being sufficient. In case the distillation process is preferred, the residue may be treated by the method to be described as a control and the results by both processes allowed to check one another.

For the work to be described solutions of ammonium vanadate were made and standardized by evaporating measured and weighed portions in a platinum crucible to dryness, and igniting in the presence of a drop of nitric acid.

The reduction with hydriodic acid was first tried; the method in general was as follows: Measured and weighed portions of the vanadate solution were placed in the Erlenmeyer breakers, the amounts of potassium iodide indicated in the tables added from a ten per cent solution and finally 10 cm^3 of a mixture of sulphuric acid and water in equal parts. The contents of the flask was then boiled until the fumes of iodine were no longer visible and the escaping steam gave no indication of free iodine with red litmus paper.* This point was reached when the volume of the liquid reached about 35 cm^3. If large amounts of potassium iodide were used the resulting color was green, owing to the presence of iodine, dissolved in hydriodic acid, with the blue tetroxide of vanadium; if smaller amounts of the iodide were used the resulting color was blue. The flasks were then removed from the flame and the contents nearly neutralized by the addition of a solution of potassium or sodium

* Gooch and Mar, Am. Jour. Sci., xxxix, p. 300. This volume, p. 19.

hydroxide,* cooled, and the neutralization completed with potassium bicarbonate in excess; care being taken to add a few drops of a tartaric acid solution to prevent the precipitation of the tetroxide. To the cooled solution a solution of iodine in potassium iodide was added in slight excess. This point can be quite easily determined, as the iodine is bleached rapidly if the solution is allowed to mix thoroughly as it is drawn from the burette into the flask. After the addition of a distinct excess of the iodine the flask should be closed with a cork coated with paraffin and allowed to stand about one-half hour. It will be noticed that at the end of about fifteen minutes the iodine has ceased to bleach, showing the oxidation to be complete. I have generally allowed the flasks to stand a few minutes longer to be sure of a complete oxidation. The

Exp.	V_2O_5 taken.	V_2O_5 found.	Error.	Amount KI.	Amount $H_2SO_4(1-1)$
	grm.	grm.	grm.	grm.	cm^3
(1)	0.1699	0.1690	0.0009–	1	10
(2)	0.1704	0.1699	0.0005–	1	10
(3)	0.1706	0.1700	0.0006–	1	10
(4)	0.1702	0.1692	0.0010–	1	10
(5)	0.3613	0.3620	0.0007+	1.5	10
(6)	0.1805	0.1803	0.0002–	1	10
(7)	0.3614	0.3620	0.0006+	1.5	10
(8)	0.1811	0.1814	0.0003+	1	10
(9)	0.1807	0.1815	0.0008+	1	10
(10)	0.3613	0.3620	0.0007+	1.5	10
(11)	0.3679	0.3674	0.0005–	1.5	10
(12)	0.3612	0.3608	0.0004–	1.5	10
(13)	0.2893	0.2907	0.0014+	1.5	10
(14)	0.3456	0.3448	0.0008–	1.5	10
(15)	0.3453	0.3448	0.0005–	1.5	10
(16)	0.3907	0.3912	0.0005+	2	10
(17)	0.3908	0.3898	0.0010–	1	10
(18)	0.3906	0.3921	0.0015+	2	10
(19)	0.3909	0.3912	0.0003+	1.5	10

excess of iodine is then destroyed by standard arsenious acid solution, against which the iodine has been previously stan-

* The potassium or sodium hydroxide for this work must be free from alcohol, as the solution is allowed to stand with iodine after neutralization. It was prepared by mixing potassium or sodium carbonate in proper proportions with calcium oxide and filtering off the calcium carbonate.

dardized, starch added and the color brought back with a few drops of iodine. The amount of arsenious acid solution used for the bleaching of the iodine, in terms of iodine subtracted from the whole amount of iodine used, gives the amount of iodine necessary to oxidize the vanadium from the condition of tetroxide to that of pentoxide. The results are given in the preceding table.

The results are on the whole satisfactory, the average error of all the determinations being less than 0.0002 —. It will be noticed that large amounts of potassium iodide tend to give plus errors.

The action of the hydrobromic acid was tried in exactly the same manner. It was found that when the residual volume of the liquid in the flask reached 25 cm³ the blue color appeared, and the absence of free bromine was proved by holding a paper moistened with potassium iodide in the steam. If the boiling is not carried to the point indicated, where the blue color appears, the results come low, showing incomplete reduction. The results follow in the table.

Exp.	V_2O_5 taken.	V_2O_5 taken.	Error.	Amount KBr.	Amount $H_2SO_4(1^{-1})$
	grm.	grm.	grm.	grm.	cm³
(1)	0.1890	0.1876	0.0014—	1	10
(2)	0.1886	0.1886	0.0000	2	10
(3)	0.1885	0.1882	0.0003—	1	10
(4)	0.1885	0.1886	0.0001+	1.5	10
(5)	0.1881	0.1873	0.0008—	1.5	10
(6)	0.1886	0.1882	0.0004—	2	10
(7)	0.3907	0.3894	0.0013—	2	10
(8)	0.3907	0.3903	0.0004—	2	10
(9)	0.3907	0.3894	0.0013—	2	10
(10)	0.3909	0.3889	0.0020—	2	10
(11)	0.3911	0.3903	0.0008—	1.5	10
(12)	0.3902	0.3900	0.0002—	2.5	10
Average error of series = 0.0007—.					

LVIII

THE SEPARATION AND IDENTIFICATION OF POTASSIUM AND SODIUM.

By D. ALBERT KREIDER and J. E. BRECKENRIDGE.*

THE application of the spectroscope to the detection of potassium and sodium, for which there has thus far been no alternative, is not so unsatisfactory in the evidence as to the presence or absence of these elements as it is in its utter failure, except under delicate quantitative comparisons, to give any idea as to the quantity of either element indicated; and since the most minute quantity of either element is sufficient to produce its characteristic line in the spectroscope, together with the fact that so many of the reagents employed in analysis contain a trace of alkali, the indication of the spectroscope is rendered misleading. While to the careful observer the presence or absence of potassium is invariably revealed, all evidence as to the ubiquitous element sodium is practically worthless. It has, therefore, appeared advisable to us to undertake the following work looking toward a method for the direct determination of sodium based upon the principle of the perchlorate method for the quantitative determination of potassium. The fact that, in the form of the perchlorate, potassium is insoluble while sodium is readily soluble in 97 per cent alcohol, affords a means for the separation of the two elements as well as for the identification of the former. By converting the sodium in the filtrate from the precipitated potassium salt either to the chloride or sulphate, in which forms it is insoluble in alcohol, a means for the detection of sodium is also provided.

Assured by the experiments previously published by one of

* From Am. Jour. Sci., ii, 263.

us,* that the determination of potassium according to this method would be sufficiently accurate, our experimentation was directed towards determining the conditions of greatest utility and delicacy for the detection of sodium. In converting the sodium from the perchlorate to the chloride, attempts were first made to substitute some soluble chloride for the free acid, the addition of which to the alcoholic solution of sodium perchlorate, it was feared, might result in the formation of the dangerously explosive compound, perchloric ether. But aniline hydrochloride, prepared by saturating a solution of aniline in absolute alcohol with gaseous hydrochloric acid, when applied to the precipitation of 0.010 grm. of sodium perchlorate dissolved in 5 cm^3 of 97 per cent alcohol, proved so hopelessly inadequate that we resorted immediately to the use of free acid, which, fortunately, was found perfectly safe even in the presence of considerable perchloric acid and at the boiling point of the mixture.

The strongest aqueous solution of hydrochloric acid, however, is inapplicable, as was proved by several experiments in which as much as 0.010 grm. of sodium perchlorate, dissolved in only 5 cm^3 of 97 per cent alcohol, failed to be revealed by the addition of the strongest aqueous solution of the acid, added in quantities varying from a single drop to 10 cm^3 — not the slightest turbidity being produced. By substituting for the aqueous solution of the acid, a saturated solution of hydrochloric acid in 97 per cent alcohol, of which 5 cm^3 were used for the precipitation, quantities of from 0.002 to 0.003 grm. of sodium perchlorate dissolved in 5 cm^3 of 97 per cent alcohol could be detected with certainty; but this could not be made sufficiently delicate. Concentrated sulphuric acid was also applied as the precipitant and was found reliable for quantities of about 0.003 grm. of sodium perchlorate dissolved in 10 cm^3 of 97 per cent alcohol, when a single drop of the acid was added, but an excess of the acid caused the precipitate to redissolve. Gaseous hydrochloric acid proved most effectual. The dehydrating effect of the acid upon the alcohol greatly

* Kreider, Am. Jour. Sci., vol. xlix, 448. This volume, p. 282.

increases the insolubility of sodium and secures a remarkable delicacy, as is evident from the results recorded in Table I.

TABLE I.

$NaClO_4$ taken.	Na_2O equivalent.	97% alcohol.	Indication.
grm.	grm.	cm^3	
0.0100	0.00250	10	Very strong.
0.0050	0.00125	10	Strong.
0.0040	0.00100	10	Strong.
0.0030	0.00075	10	Strong.
0.0030	0.00075	10	Good.
0.0020	0.00050	10	Good.
0.0020	0.00050	10	Good.
0.0010	0.00025	10	Good.
0.0005	0.00012	10	Trace.
0.0003	0.00006	10	Trace.
0.0001	0.00003	10	None.
0.0000	0.00000	10	None.
0.0010	0.00025	40	Distinct.

The sodium employed in these determinations was in the form of perchlorate, prepared by evaporating sodium chloride, free of potassium and ammonium, with perchloric acid until tests for hydrochloric acid proved a complete conversion to the perchlorate, when the excess of acid was volatilized by heating over a drying cone. Two grams of this purified salt were dissolved in 200 cm^3 of 97 per cent alcohol and served for our standard solution for those tests in which quantities greater than 0.001 grm. of sodium perchlorate were used. When it appeared evident that smaller quantities could be detected with certainty, a solution of the salt containing 0.050 grm. per 100 cm^3 of water was used, and each portion evaporated to dryness before adding the alcohol. In each case the alcohol subsequent to its addition was saturated with gaseous hydrochloric acid, being kept cool by immersion in a beaker of water. For the generation of hydrochloric acid, the well known form of apparatus consisting of a side-neck flask, containing sodium chloride covered with hydrochloric acid fitted with a stoppered funnel, through which sulphuric acid could be admitted as desired, served admirably.

It is evident, then, that by the use of 10 cm^3 of 97 per cent

alcohol with gaseous hydrochloric acid, 0.0008 grm. of sodium oxide can be found with certainty; and when the alcohol is allowed to become saturated with the gas even 0.00006 grm. of sodium oxide will be unmistakably revealed. The quantity of alcohol, 10 cm^3, is sufficient for all purposes, since this amount will dissolve about two grams of sodium perchlorate; but even in 40 cm^3 0.0002 grm. of sodium oxide may be seen distinctly; from which fact it is evident that this method can be applied to the quantitative determination of sodium. Absolute alcohol does not materially increase the delicacy of the test.

In Table II are recorded the results of experiments made upon mixtures of the two elements. The sodium and potassium taken were drawn from separate standard solutions containing one gram of the purified perchlorates in 100 cm^3 of distilled water. After evaporating to dryness on the steam bath, the residue was treated with the usual amount of 97 per cent alcohol, the insoluble potassium perchlorate was removed by filtering through a dry paper filter and dry funnel into a dry test-tube, and the filtrate saturated with gaseous hydrochloric acid.

TABLE II.

$KClO_4$ taken.	K_2O equivalent.	$NaClO_4$ taken.	Na_2O equivalent.	Indication for potassium.	Indication for sodium.
grm.	grm.	grm.	grm.		
0.0500	0.01699	0.0500	0.01250	Strong.	Strong.
0.0200	0.00680	0.0200	0.00500	Strong.	Strong.
0.0100	0.00340	0.0100	0.00250	Strong.	Strong.
0.0050	0.00170	0.0050	0.00125	Strong.	Strong.
0.0040	0.00136	0.0040	0.00100	Good.	Good.
0.0030	0.00102	0.0030	0.00075	Good.	Good.
0.0020	0.00068	0.0020	0.00050	Good.	Good.
0.0010	0.00034	0.0010	0.00025	Good.	Good.
0.0005	0.00017	0.0005	0.00012	Trace.	Trace.
0.0003	0.00010	0.0003	0.00007	Trace.	Trace.
0.0001	0.00003	0.0001	0.00003	Faintest trace.	None.
0.0000	0.00000	0.0100	0.00250	None.	Strong.
0.0100	0.00340	0.0000	0.00000	Strong.	None.

These results prove that the two elements when combined in any proportion may be separated and identified with great delicacy.

Before applying this method, however, it is necessary to remove certain interfering substances. While potassium may be safely tested for in the presence of other bases and acids, except ammonium, cæsium, and rubidium, and sulphuric acid* the large number of elements whose chlorides are insoluble in alcohol necessitates their removal before testing for sodium. But among the common alkalies ammonium is the only one whose presence is objectionable. Lithium does not affect either the test for potassium or sodium, as was determined by an experiment in which about 0.1 grm. of lithium chloride was converted into the perchlorate by evaporating with an excess of perchloric acid and treated with 10 cm^3 of 97 per cent alcohol. A perfectly clear solution was obtained, which upon saturation with gaseous hydrochloric acid and cooling, remained clear. The removal of sulphuric acid is necessitated by the insolubility of sodium sulphate in alcohol.

TABLE III.

Bases taken Pb. Cu. Al. Fe. Zn. Ba. Ca. and Mg. as nitrates.	K_2O taken.	Na_2O taken.	Indication for potassium.	Indication for sodium.
grm.	grm.	grm.		
0.0500 of each	0.0000	0.0000	Faintest trace.	Trace.
0.0500 "	0.0017	0.0012	Good.	Good.
0.1000 "	0.0000	0.0000	Faintest trace.	Trace.
0.1000 "	0.0000	0.0005	Faintest trace.	Good.

In the experiments made with potassium and sodium associated with other acids and bases, the results of which are recorded in Table III, the following treatment was adopted. The several groups of bases were successively removed in the ordinary way: Hydrogen sulphide in ammoniacal solution removed the lead, mercury, copper and zinc. Barium and calcium were removed by ammonium carbonate, the final filtrate being evaporated and ignited to the complete volatilization of ammonia. The residue was dissolved and treated with barium hydrate for the removal of m[illegible]esium, and after filtering the barium was again [illegible]ium carbonate and the

filtrate evaporated and ignited as before. This residue was then treated with 10 cm^3 of boiling water and after stirring was filtered in order to remove the organic matter usually found at this stage of the treatment. To the filtrate was added 0.1 to 0.5 cm^3 of pure perchloric acid, about 1.7 sp. gr., according to the amount of residue, and evaporated over the steam bath until the white fumes of perchloric acid appeared. When the quantity of sodium is large it is safer to evaporate several times in order to secure a complete conversion to the perchlorate, and in such case precautions must be taken to have sufficient of the acid present. Upon treating with 97 per cent alcohol the presence of potassium is revealed by an insoluble residue. This is removed by a dry filter and the filtrate saturated with gaseous hydrochloric acid, whereupon sodium, if originally present in amount greater than 0.0005 grm. of the oxide, will be precipitated in granular condition.

The fact that minute traces of sodium and potassium are found in the blank tests is to be expected from the delicacy of the method as proved by Tables I and II, when it is remembered that but very few of the so-called chemically pure reagents are absolutely free of sodium and that even distilled water kept in glass vessels contains a trace of the alkaline elements. However, the indication for sodium in the blank tests appeared only as a cloudiness and after complete saturation, while when the quantity of sodium oxide present is not less than 0.0005 the precipitate appears in granular form and before the alcohol is completely saturated, which leaves the method all that could be desired for qualitative determinations.

Preparation of the Perchloric Acid. — The perchloric acid prepared according to the method previously published by one of us,* by converting sodium chlorate into the perchlorate by heat, destroying the residual chlorate by treating with the strongest hydrochloric acid, from which the sodium chloride was separated by filtering through a Gooch filter and the excess of hydrochloric acid removed by evaporation — while answering perfectly well for the detection of potassium, is inap-

* Krieder, Am. Jour. Sci., vol. xlix, 443. This volume p. 282.

plicable to the test for sodium, because of the small amount of this element which the acid always contains due to the partial solubility of sodium chloride in hydrochloric acid. As distillation seems the only method for the removal of this residual sodium, our attention was given to a study of the best conditions for the distillation. Various experiments led to the adoption of the following treatment, which we found in every case perfectly safe and fairly rapid. To prevent loss by decomposition the distillation must be carried on under diminished pressure, and unless the acid has been previously concentrated by evaporating until the white fumes appear, if there is any considerable amount of the acid in the distilling flask, even with porcelain chips to check it, it bumps with such violence as to throw the liquid to all parts of the flask and possibly into the condenser. It appeared to be essential, therefore, to start with only a small amount of the concentrated acid in an apparatus which would permit of the gradual addition of the acid without relieving the vacuum. Rubber stoppers or connectors are not advisably used where the acid may condense upon them and flow back into the flask. Invariably oxidizable matter is carried back, causing explosions which vary in force and seriousness according to circumstances.

We, therefore, selected a strong distilling flask of about 100 cm^3 capacity and sealed into the tubulation a stoppered funnel which reached well into the bulb. The stop-cock of this funnel was carefully cleansed of vaseline and lubricated with metaphosphoric acid obtained by boiling syrupy orthophosphoric acid until the temperature of 350° C. had been attained.* The side neck of the flask was inclined upward for a short distance before being bent into the receiver, with which it was connected by a rubber stopper through which the tube extended for a safe distance. An ordinary bottle of 250 cm^3 capacity served for a receiver and was closed by a doubly perforated stopper. Through one of the perforations

* This lubricant will be found entirely satisfactory and greatly preferable to vaseline in many other operations where the greasy effect of the latter is objectionable.

the adapter from the condenser was entered; through the other, connection was made with a small glass bulb inserted between the receiver and the next tube, containing moistened sticks of caustic potash, in order to prevent the potash from reaching the receiver in case of an accident to the pump. The object of the potash was to absorb any chlorine resulting from the inevitable slight decomposition of the acid, and thus to protect the mercury of the pump. For the exhaustion an automatic pump was employed and generally twenty minutes would suffice to reduce the pressure to about 8 mm., when the distillation was begun. The pump gradually reduced the pressure, which was kept at about 3 to 5 mm. The bottom of the distilling flask was covered with a layer of fine porcelain chips to a depth of about 1 cm^3 and the whole flask was surrounded by a cylinder of thin sheet iron closed below, while the upper opening was protected by an asbestos cover. By this means heat was uniformly applied to every part of the flask and up to the point at which, if the acid condensed, it would flow into the receiver. Three or 4 cm^3 of the acid were admitted to the flask, after which the temperature was raised to about 130° C. and the acid admitted at about the same rate that it dropped from the condenser, care being taken to prevent the liquid in the distilling flask from disappearing entirely. No danger was experienced in admitting the acid; the porcelain chips distribute the heat and prevent the colder acid from reaching the glass.

Careful compliance with the above conditions will secure satisfactory results. As a rule we succeeded in distilling at the rate of 25 cm^3 to 40 cm^3 per hour, and when it is remembered that the product is the dihydrate of perchloric acid, the most concentrated form in which it is stable, and of which 0.1 grm. of potassium oxide requires only 0.16 cm^3, it will be seen that by this process the acid may be prepared without great difficulty.

LIX

ON THE ESTIMATION OF CADMIUM AS THE OXIDE.

By PHILIP E. BROWNING and LOUIS C. JONES.*

In an article entitled "The Estimation of Cadmium" † Max Muspratt discusses critically some of the methods in use for the determination of that element. Muspratt finds that the method which involves the precipitation as carbonate, ignition and weighing as oxide gives low results, and he accounts for these results by the well known tendency of cadmium to reduction, especially in the presence of organic matter. To avoid this reduction he dissolved the precipitated carbonate in nitric acid, evaporated to dryness on a water bath, and gently ignited the nitrate to the condition of the oxide. This treatment also gave low results, although the oxide obtained from the ignition of the nitrate was found to contain traces of sulphate from the solution of the cadmium sulphate used. A second method of treatment was to filter and dry the precipitated carbonate and remove as much of it as possible to a weighed porcelain crucible, ignite, and weigh by itself. This oxide was found to be free from traces of sulphate.‡

The remainder of the cadmium oxide adhering to the paper was dissolved in pure nitric acid and the solution and rinsings evaporated to dryness and ignited in a weighed crucible and weighed. Here also low results were obtained which, after the extended process of manipulation, would scarcely seem surprising. If, however, Muspratt adds, the oxide obtained

* From Am. Jour. Sci., ii, 269.

† Jour. Sci. Chem. Ind., xiii, 211.

‡ Muspratt's theory is that in the ignition of the carbonate the sulphate is dissociated, while the ignition of the nitrate does not effect this result.

from the ignition of the carbonate be taken as Cd_2O the results are satisfactory.

A third modification gives more satisfactory results. The method of treatment is the same as the last mentioned, except that the oxide obtained from the ignition of the carbonate is ignited in a stream of oxygen until no further increase in weight results.

In a former paper from this laboratory * one of us made use of the carbonate method for the determination of cadmium after having separated that metal from copper. The filtration was made on asbestos in a Gooch crucible and the results were most satisfactory. The object of the work to be described is to show that when the carbonate is filtered upon an asbestos felt previously ignited the dangers of reduction are obviated and the carbonate process is both simplified and placed among good analytical methods. The solution used for the work was one of cadmium sulphate, and the standard was determined by evaporating measured and weighed portions to dryness in the presence of a few drops of sulphuric acid, igniting at low redness, and weighing as the anhydrous sulphate. The average of several closely agreeing results was taken as the standard. Measured and weighed portions of this solution were diluted to about 300 cm^3 with hot water and a solution of potassium carbonate, 10 per cent, added drop by drop with constant stirring until no further precipitate was obtained. The precipitate was then boiled for about fifteen minutes, when it became granular and settled quickly. It was then filtered upon asbestos, washed thoroughly, dried, and ignited at red heat until a constant weight was obtained. In several instances the weighed oxide was treated with a drop of nitric acid, again ignited and weighed, but in no case was there a perceptible change in weight. In the following table the results are tabulated.

As will be noticed, the results show a plus error which might naturally be due to a slight inclusion of the alkali carbonate. To test the truth of this hypothesis, a portion of

* Browning, Am. Jour. Sci., xlvi, 280. This volume, p. 226.

Exp.	CdO taken.	CdO found.	Error.
	grm.	grm.	grm.
(1)	0.1140	0.1143	0.0003+
(2)	0.1142	0.1137	0.0005—
(3)	0.1141	0.1148	0.0007+
(4)	0.1141	0.1148	0.0007+
(5)	0.1142	0.1146	0.0004+
(6)	0.1143	0.1147	0.0004+
(7)	0.1143	0.1144	0.0001+
(8)	0.1139	0.1146	0.0007+
(9)	0.1270	0.1272	0.0002+
(10)	0.1279	0.1283	0.0004+
(11)	0.1272	0.1281	0.0009+
(12)	0.1278	0.1281	0.0003+
(13)	0.2556	0.2561	0.0005+
(14)	0.2550	0.2547	0.0003—
(15)	0.1272	0.1279	0.0007+
(16)	0.1281	0.1288	0.0007+
(17)	0.1274	0.1278	0.0004+
(18)	0.1284	0.1290	0.0006+
(19)	0.1271	0.1277	0.0006+
(20)	0.1278	0.1285	0.0007+
(21)	0.2555	0.2555	0.0000

the oxide which gave a plus error of 0.0007 grm. was dissolved and tested for potassium by the perchloric acid method * and an amount of that element was found equal to 0.0006 grm. of the carbonate. Another portion of the oxide which showed no error was similarly treated and only 0.0002 grm. of the carbonate was found. The results show, as we think, that the carbonate method can be successfully applied to the quantitative estimation of cadmium without recourse to the tedious process of manipulation recommended by Muspratt.

* Kreider, Am. Jour. Sci., xlix, 443. This volume, p. 282.

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